Dissertation
submitted to the
Combined Faculties for the Natural Sciences and for Mathematics
of the Ruperto-Carola University of Heidelberg, Germany
for the degree of
Doctor of Natural Sciences

Put forward by
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Born in Borås, Sweden (Gustav Adolf Parish)
Oral examination: 18.11.2015

QED Corrections to Atomic Wavefunctions in Highly Charged Ions

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Abstract

Bound electron states in highly charged ions are strongly influenced by the effects of relativity and quantum electrodynamics (QED). These effects induce shifts of the binding energies as well as corrections to observables related to atomic processes. In this work a numerical procedure is described and implemented in which the QED effects are treated as corrections to relativistic bound-state wavefunctions. This approach, which is based on the recently developed *covariant evolution-operator formalism*, allows for a merging of QED with the standard methods of many-body perturbation theory. In particular, it enables an evaluation of the combined effect of QED and electron correlation in few-electron systems. Numerical results for this effect are presented for the ground state energy of heliumlike ions. A detailed analysis of the contribution from the electron self-energy is carried out in both the Feynman and Coulomb gauge. It is found that the Feynman gauge suffers from large numerical cancellations and aquires significant contributions from terms involving multiple interactions with the nuclear potential (the so-called *many-potential terms*), while the Coulomb gauge is well suited for an approximate treatment based on terms involving only freely propagating electrons (the *zero-potential terms*).

With the help of QED-corrected wavefunctions it is also possible to compute corrections to observables in basic atomic processes. In this work some of the one-loop QED corrections (those derivable from perturbed wavefunctions and energies) to the differential cross section and distribution of polarization in radiative recombination of initially bare uranium nuclei are evaluated, as well as the corresponding corrections to the ratio τ_{E1}/τ_{M2} of the electric dipole and magnetic quadrupole transition amplitudes in the $2p_{3/2} \to 1s$ radiative decay of hydrogenlike uranium. The results from these calculations are all of the expected magnitude, namely on the order of the fine-structure contant α.

Zusammenfassung

Die gebundenen Zustände von Elektronen in hochgeladenen Ionen werden stark von den Effekten der Relativitätstheorie und der Quantenelektrodynamik (QED) beeinflusst. Diese Effekte induzieren korrekturen an Bindungsenergien der Elektronen sowie Observablen atomarer Prozesse. In dieser Arbeit wird ein numerisches Verfahren beschrieben und implementiert in welchem die QED-Effekte als Korrekturen gebundener relativistischer Wellenfunktionen behandelt werden. Dieser Ansatz, der auf dem kürzlich entwickelten *covariant evolution-operator formalism* basiert, ermöglicht eine Zusammenführung von QED mit den Standardmethoden der Vielteilchen-Störungstheorie. Insbesondere ermöglicht es eine Bewertung des kombinierten Effekts von QED und Elektronenkorrelationen in Wenig-Elektronensystemen. Numerische Ergebnisse für diesen Effekt werden für die Grundzustandsenergie von Helium-ähnlichen Ionen präsentiert. Eine detaillierte Analyse des Beitrags von der Elektronenselbstenergie wird sowohl in der Feynman- und Coulomb-Eichung durchgeführt. Es wird gezeigt, dass die Feynman-Eichung unter großen numerischen Aufhebungen leidet und signifikante Beiträge von Termen, die mehrere Interaktionen mit dem Kernpotential beinhalten (die so genannten *Vielpotentialterme*), enthält. Wohingegen die Coulomb-Eichung für eine ungefähre Behandlung, welche auf den Termen mit freien Elektronenpropagatoren (die *Nullpotentialterme*) basiert, geeignet ist.

Mit Hilfe von QED korrigierten Wellenfunktionen ist es auch möglich, Korrekturen an den Observablen in atomaren Prozesse zu berechnen. In dieser Arbeit wurden einige der Einschleifen-QED Korrekturen (ableitbar von gestörten Wellenfunktionen und Energien) zu dem Differentiellen Wirkungsquerschnitt und der Verteilung der Polarisation in der Radiativen Rekombination von zunächst nackten Urankernen ausgewertet, als auch die entsprechende Korrekturen zu dem Verhältnis τ_{E1}/τ_{M2} der elektrischen Dipol und der magnetischen Quadrupol Übergangsamplituden in dem $2p_{3/2} \to 1s$ strahlenden Zerfall des Wasserstoff-änlichen Urans. Die Ergebnisse dieser Berechnungen sind alle der erwarteten Größenordnung, nämlich in der der Feinstrukturkonstante α.

Dedikeras till Emelie och Ture
Dedicated to Emelie and Ture

Publications

The author has contributed to the following publications during the doctoral studies:

- I. Lindgren, S. Salomonson, and J. Holmberg, *QED effects in scattering processes involving atomic bound states: Radiative recombination*, Phys. Rev. A **89**, 062504 (2014)
- J. Holmberg, S. Salomonson, and I. Lindgren, *Coulomb-gauge calculation of the combined effect of correlation and QED for heliumlike highly charged ions*, Phys. Rev. A **92**, 012509 (2015)
- J. Holmberg, A. N. Artemyev, A. Surzhykov, V. A. Yerokhin, and Th. Stöhlker, *QED corrections to radiative recombination and radiative decay of heavy hydrogenlike ions*, (submitted to Phys. Rev. A)

Contents

1 Introduction

Presently, the most fundamental and widely established theory for how charged particles and electromagnetic radiation interact is *quantum electrodynamics*, or QED for short. QED is a *quantum field theory*, meaning that it is formulated in terms of a set of dynamical fields — functions of space and time — whose fundamental quantum excitations correspond to the elementary particles of the theory. In QED these are the electron and its heavier cousins the muon and the tauon, as well as the photon, including their antiparticles.

The fundamental fields are coupled to each other and this means that whenever an excitation is produced in one of the fields, induced excitations will be generated in the coupled fields, and vice versa. Any given physical state is thus an incredibly intricate mixture of excitations and fluctuations in all of the coupled fields. Fortunately, however, the coupling in QED is quite weak and this means that it is perfectly justified to consider approximate states which only contain excitations of one of the fields — for example a single, isolated electron — and treat the influence from the coupled fields as corrections. In other words, the theory of QED is *perturbative*.

Since its formulation in the late 1940's [1–8], the theory of QED has been tested extensively in a large number of experiments and it has been verified to remarkable precision. For example, the theoretically predicted value of the magnetic moment of the electron coincides with the corresponding experimentally observed value to the first 12 digits [9, 10]. Already when the agreement was only at 10 digits in the 1980's, Richard Feynman, one of the originators of QED, famously compared this degree of precision to knowing the distance from New York to Los Angeles to within the width of a human hair [11]. One may rightly wonder if there really is a need for further testing of such a successful theory.

Most of the tests, however, have so far been performed in a setting where the particles can be considered as approximately free most of the time. In collision experiments, for example, particles are typically allowed to interact only in a small region of space during a short time interval, and are considered as non-interacting before and after the collision. In experiments that measure the aforementioned magnetic moment of the electron (or its heavier cousin the muon), the charged particle is confined to a closed orbit under the influence of an external magnetic field, but one typically considers the limit where the strength of the external field vanishes. Nature is however full of situations where particles are very far from being free. Indeed, most of the charged particles that surround us are held together in bound systems such as atoms or ions where a very strong interaction is present all of the time. QED should be the fundamental electromagnetic theory describing these bound systems as well, and one of the aims of current research on bound-state QED is to check to which extent the theory remains valid for these cases.

In the last couple of decades, increasing experimental and theoretical effort has been put into the study of QED of bound states in highly charged ions. Especially the development of heavy-ion facilities such as GSI in Darmstadt has enabled experiments that measure properties of such exotic ions as hydrogenlike uranium (see, e.g. [12]), where a single electron is bound to a uranium nucleus. The electron

in such an ion continuously experiences a very large electric field and this allows one to study the validity of QED in the strong-field limit. Such studies rely on an interplay between accurate theoretical predictions based on bound-state QED and precise experimental measurements.

The work described in this thesis concerns the numerical calculation of QED corrections to observable quantities related to bound states in highly charged hydrogenlike and heliumlike ions. The approach we will pursue is to evaluate the QED corrections by incorporating them directly into the bound-state wavefunctions. The main advantage of this approach, which has been developed during the last decade in a series of works by Lindgren *et al.* [13–17], is that it allows for a simultaneous treatment of QED-effects and electron correlation (loosely speaking, the fact that the motion of the electrons is significantly altered by their mutual repulsion) in few-electron ions. On its own, electron correlation can be treated accurately using many-body perturbation theory which relies upon a perturbation expansion of the atomic wavefuction, and by treating the QED effects in the same manner a sort of unification can be achieved. Using this approach we will compute the combined effect of correlation and QED in the ground state energy of heliumlike ions.

Having developed the numerical machinery for evaluating QED corrections to few-electron wavefunctions, it is straightforward to produce QED corrected single-electron wavefunctions which can be used to compute corrections to basic atomic processes involving bound states of hydrogenlike ions. Using this approach we will evaluate QED corrections to observables in the radiative recombination of initially bare uranium nuclei, as well as corrections to the $2p_{3/2} \rightarrow 1s$ radiative decay of hydrogenlike uranium.

Thesis Overview

The thesis is divided into two parts: in Part I we will present the theoretical tools needed in order to formulate a procedure for including QED effects into the atomic wavefunction. We will assume that the reader has good knowledge of quantum mechanics, classical electromagnetism, and special relativity. The well-known results from these topics will mostly be used without reference. Part II of the thesis concerns applications of the theory discussed in Part I to the computation of observable quantities in atomic physics.

Part I begins in Chapter 2 with a brief review of Dirac's relativistic single-electron theory, which is the starting point for the developments that follow. The bound-state solutions obtained in Dirac's theory will serve as zeroth-order approximations to the exact states. In Chapter 3 we review the basic results from many-body perturbation theory, which is the framework we will use for the treatment of electron correlation. Furthermore, many of the concepts introduced here will be used when we generalize the theory to include QED in later chapters. Chapter 4 concerns the basic theory of bound-state QED, and here we will define the fundamental building blocks that will be used in our combined many-body and QED treatment. Finally, in Chapter 5 we will introduce the central concepts from the recently developed framework, the *covariant evolution-operator formalism*, which allows for an inclusion of QED effects into a perturbation expansion of the bound-state wavefunction.

In Part II we will describe applications of the theory developed in Part I, as well as the numerical procedures we employ for the evaluation of the QED corrections to the atomic wavefunctions. Chapter 6 concerns the application of the combined many-body and QED treatment to the energy shift of the ground state in helium-like ions. We consider the shift due to the combination of electron correlation and single-photon QED effects. Special emphasis is placed upon the evaluation of the self-energy correction, which is the numerically most difficult to obtain. In Chapter 7 we describe how QED corrected hydrogenic wavefunctions can be used to compute corrections to transition amplitudes for two basic atomic processes — radiative recombination and radiative decay. From the corrected amplitudes we compute some of the one-loop QED corrections to the differential cross section and the angular distribution of linear polarization in the emitted radiation in radiative recombination of hydrogenlike uranium. For the same ion we also compute some of the corrections to the ratio of the $E1$ (electric dipole) and $M2$ (magnetic quadrupole) transition amplitudes in the $2p_{3/2} \to 1s$ radiative decay, a quantity to which experimental access has recently been demonstrated [18]. Chapter 8 is devoted to the presentation and discussion of our results, and we end with a summary and brief outlook in Chapter 9.

Notation and units

Throughout most of the thesis we will employ so-called *natural units* which are defined such that the reduced Planck's constant $\hbar$, the permittivity of free space ϵ_0, and the speed of light c all take the numerical value 1. Some of our results will be given in other units, which will then be explicitly stated.

In relativistic notation, four-vectors are written as a^μ, or simply a when not referring to a particular component. Spatial vectors are written in boldface, such as $\mathbf{a}$. In some parts of the thesis, particularly in Part II where we discuss applications and their numerical implementation, we shall use the notation $p = |\mathbf{p}| = \sqrt{\mathbf{p}^2}$, which will be explicitly stated.

Greek indices μ, ν, λ etc. range from 0 to 3 while Latin indices i, j, k etc. range from 1 to 3 and refer to the spatial part of four-vectors. Summation is implied whenever an index is repeated twice in the same term, once lowered and once raised.

The metric tensor $g^{\mu\nu}$ is taken to be

$$g = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. \tag{1.1}$$

This tensor relates a covariant four-vector $a_\mu = (a^0, -\mathbf{a})$ to its contravariant counterpart $a^\mu = (a^0, \mathbf{a})$ through

$$a^\mu = g^{\mu\nu} a_\nu. \tag{1.2}$$

The dot product between four-vectors is written as

$$a \cdot b = a_\mu b^\mu = g_{\mu\nu} a^\nu b^\mu = a^0 b^0 - \mathbf{a} \cdot \mathbf{b}, \tag{1.3}$$

and the derivative operator is written as

$$\partial_\mu = \frac{\partial}{\partial x^\mu} = \left(\frac{\partial}{\partial t}, \nabla \right). \tag{1.4}$$

A Note About Computational Resources

The numerical method employed in the computation of the QED corrections in this work requires the evaluation of integrals involving functions which are only known numerically. In combination with large summations over intermediate states this means that the computations quickly become quite resource-intensive; this is especially true of the so-called self-energy correction which involves multidimensional numerical integrals.

A typical computation in this work required the use of around 1000 to 10000 core-hours at a processor frequency of 2.27 GHz. If these computations were to be carried out using only a single processor, one would thus have to wait over a year for the results to arrive (meanwhile hoping that one did not make any mistakes). By the use of parallell computing the computations can be divided into subtasks which are distributed among several processors and performed simultaneously. Using 100 cores the results can instead be obtained in a few days.

The computations in this work were performed on resources at Chalmers Centre for Computational Science and Engineering (C3SE) provided by the Swedish National Infrastructure for Computing (SNIC).

Part I
Theoretical Background

In this first part of the thesis we will review the theoretical foundations which form the basis for the applications that will be described in Part II. Most of the material we will present here is fairly well known and can be considered as standard. The exception is Chapter 5 which deals with the recently developed "covariant evolution-operator formalism" intended to unify many-body perturbation theory and quantum electrodynamics.

2 Atomic States in Dirac Theory

We will in this thesis be concerned with quantum-electrodynamic (QED) corrections to bound states in highly charged one- and two-electron ions. Our starting point for these corrections — the zeroth-order approximation to the exact problem — will be Dirac's relativistic quantum theory of the electron [19]. Dirac originally proposed his equation as a relativistic generalization of the non-relativistic Schrödinger equation, that is, a quantum-mechanical equation governing a single particle. Later, with the advent of quantum field theory, the equation was reinterpreted as the classical field equation describing elementary spin $\frac{1}{2}$ fields, its solutions subject to *second quantization* with the resulting possibility for particle creation and annihilation. In this section we will follow Dirac's original interpretation and return to quantum field theory later on.

2.1 The Dirac Equation

In manifestly covariant form, the time-dependent Dirac equation for an electron of mass m in free space is

$$(i\gamma^\mu \partial_\mu - m)\psi(x) = 0 \tag{2.1}$$

where γ^μ are the 4×4 Dirac gamma matrices satisfying the anticommutation relation

$$\gamma^\mu\gamma^\nu + \gamma^\nu\gamma^\mu \equiv \{\gamma^\mu, \gamma^\nu\} = 2g^{\mu\nu}. \tag{2.2}$$

This relation is required in order for Eq. (2.1) to fulfill the relativistic energy-momentum relation $E^2 = \mathbf{p}^2 + m^2$. The explicit representation of the gamma matrices is a matter of convention; we will in this work use the *Dirac representation*:

$$\gamma^0 = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{2.3}$$

$$\gamma^1 = \begin{pmatrix} \mathbf{0} & \sigma^1 \\ -\sigma^1 & \mathbf{0} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix} \tag{2.4}$$

$$\gamma^2 = \begin{pmatrix} \mathbf{0} & \sigma^2 \\ -\sigma^2 & \mathbf{0} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \end{pmatrix} \tag{2.5}$$

$$\gamma^3 = \begin{pmatrix} \mathbf{0} & \sigma^3 \\ -\sigma^3 & \mathbf{0} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}. \tag{2.6}$$

The appearance of the 2×2 Pauli spin-matrices σ^i here reflects the fact that the Dirac equation incorporates the spin $\frac{1}{2}$ degree of freedom from the very beginning, as a direct consequence of the merging of quantum theory and relativity.

The Dirac equation (2.1) has plane-wave solutions of the form (see, e.g., [20])

$$\begin{aligned}\psi(x) &\propto u_r(\mathbf{p})e^{-ip\cdot x},\\ \psi(x) &\propto v_r(\mathbf{p})e^{ip\cdot x}\end{aligned} \tag{2.7}$$

where $u_r(\mathbf{p})$ and $v_r(\mathbf{p})$ are 4×1 vectors and where the index $r = 1, 2$. For each $\mathbf{p}$ there are thus four independent solutions — two with positive energy $p^0 = +\sqrt{m^2+\mathbf{p}^2}$ and two with negative energy $p^0 = -\sqrt{m^2+\mathbf{p}^2}$. The further duplicity of each energy-solution is related to the spin of the electron, and one can choose $u_r(\mathbf{p})$ and $v_r(\mathbf{p})$ to be eigenvectors of spin $\frac{1}{2}$. The negative-energy solutions can be reinterpreted to describe the (positive-energy) states of the antiparticle of the electron — the positron.

The interaction of the electric charge $-e$ of the electron with an external electromagnetic field given by the four-potential $A^\mu = (\phi, \mathbf{A})$ can be described via the so-called *minimal substitution*, where the four-momentum p^μ of the electron is substituted with (see e.g. [21]):

$$p^\mu \to p^\mu + eA^\mu. \tag{2.8}$$

Identification of the four-momentum operator $\hat{p}_\mu = i\partial_\mu$ in (2.1) gives, together with (2.8), the Dirac equation in the presence of an external electromagnetic field:

$$[i\gamma^\mu(\partial_\mu - ieA_\mu) - m]\psi(x) = 0. \tag{2.9}$$

The manifestly covariant forms (2.1) and (2.9) are convenient for studies which rely heavily on relativistic covariance. However, in most atomic physics applications there is a naturally preferred reference system — the one in which the atomic nucleus is at rest — and in this case explicit relativistic covariance is not essential. Indeed, since we will mainly be interested in energy eigenfunctions (stationary solutions), it is quite natural to express the equations instead in terms of the Dirac α and β matrices defined by

$$\beta = \gamma^0, \qquad \alpha^i = \gamma^0\gamma^i. \tag{2.10}$$

Multiplying the Dirac equation in an external field (2.9) from the left by γ^0 we obtain the equivalent equation

$$(i\partial_t + i\boldsymbol{\alpha}\cdot\nabla + e\phi - e\boldsymbol{\alpha}\cdot\mathbf{A} - \beta m)\psi(x) = 0. \tag{2.11}$$

Sometimes we will use a fourth α matrix $\alpha^0 = \gamma^0\gamma^0 = 1$ in order to retain an explicitly covariant notation in terms of α^μ.

For energy eigenstates the operator $i\partial_t$ simply gives the energy eigenvalue and the remaining part of (2.11) is the (negative of the) Dirac hamiltonian:

$$H_{\mathrm{D}} = -i\boldsymbol{\alpha}\cdot\nabla - e\phi + e\boldsymbol{\alpha}\cdot\mathbf{A} + \beta m. \tag{2.12}$$

By choosing $\mathbf{A} = 0$ and $\phi = V_{\mathrm{nuc.}}$ to be the electrostatic potential from the atomic nucleus, the stationary Dirac equation becomes

$$(-i\boldsymbol{\alpha}\cdot\nabla - eV_{\mathrm{nuc.}} + \beta m)\Phi(\mathbf{x}) = E\Phi(\mathbf{x}) \tag{2.13}$$

and this equation will be the starting point for our description of a single relativistic atomic electron.

2.2 Hydrogenic Solutions to the Dirac Equation

Disregarding very small corrections from inhomogeneities of the nuclear charge distribution, the electrostatic potential from an atomic nucleus is spherically symmetric. The energy eigenfunctions which are solutions to Eq. (2.13) can then be written in terms of the spherical coordinates r, θ, φ as [22]

$$\Phi(r,\theta,\varphi) = \frac{1}{r}\begin{pmatrix} F(r)\chi_{\kappa}^{m_j}(\theta,\varphi) \\ iG(r)\chi_{-\kappa}^{m_j}(\theta,\varphi) \end{pmatrix} \tag{2.14}$$

where F and G are known as the *large* and *small radial components*, respectively. The two-component objects χ are ls-coupled spherical spinors:

$$\chi_{\kappa}^{m_j}(\theta,\varphi) = \sum_{m_l,m_s} \langle l m_l, \tfrac{1}{2} m_s | j m_j \rangle Y_{m_l}^{l}(\theta,\varphi)\xi_{m_s} \tag{2.15}$$

where $\langle j_1 m_1, j_2 m_2 | J M \rangle$ is a Clebsch-Gordan coefficient, Y_m^l are the spherical harmonics, and the spin eigenvectors are given by

$$\xi_{\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad \xi_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{2.16}$$

The large and small components are associated with the same total angular momentum j, but differ by one unit in the orbital angular momentum l. Normally states are labelled according to the l-value of the large component, often in spectroscopic notation (s for $l = 0$, p for $l = 1$, etc.). The spin-angular quantum number $\kappa = (-1)^{j+l+\frac{1}{2}}(j + \frac{1}{2})$ is given by the total angular-momentum quantum number j and the orbital angular-momentum quantum number l of the large component. The projection of j onto the z-axis is given by m_j. In the non-relativistic limit the small component G normally vanishes and F plays the role of the wavefunction in non-relativistic quantum mechanics.

Consider now an atomic nucleus of charge $+Ze$. If the nucleus can be considered point-like the electrostatic potential $V_{\text{nuc.}}$ is simply given by $Ze/4\pi r$ and the solutions can then be obtained analytically (see, e.g. [22]). The energy eigenvalues belong to one of the following three categories: 1) the negative-energy solutions with $E < -m$ which form a continuum and represent positron states, 2) for $0 < E < m$ the solutions form a countable set and represent electron states which are bound by the nuclear potential, and 3) the solutions with $m < E$ are unbound electron states which lie in the positive-energy continuum.

The hydrogenic bound-state energies are well-known and given by

$$E_{n,\kappa} = m\left[1 + \left(\frac{Z\alpha}{n - |\kappa| + \sqrt{\kappa^2 - Z^2\alpha^2}}\right)^2\right]^{-\frac{1}{2}} \tag{2.17}$$

where $\alpha = e^2/4\pi \approx 1/137.036...$ is the fine-structure constant and $n = 1, 2, 3, ...$ is the principal quantum number. The energy eigenvalues do not depend on the projection m_j, which is a consequence of the spherical symmetry of the problem.

An interesting feature of Eq. (2.17) is that it is independent of the sign of κ. This means that there should be complete degeneracy between states with the same

principal quantum number n and total angular momentum j, but which differ by one unit in the orbital angular momentum l. For example, the $2s$ ($n = 2$, $l = 0$, $j = 1/2$, $\kappa = -1$) and $2p_{1/2}$ ($n = 2$, $l = 1$, $j = 1/2$, $\kappa = 1$) states should have the exact same energy according to Dirac theory. The empirically observed difference in energy between these states are due to the so-called *Lamb shift*, named after Willis Lamb who together with Robert Retherford was the first to clearly demonstrate its existence in experiment in 1947 [23]. The Lamb shift comes about because of the self-interaction of the bound electron via the electromagnetic field as well as the self-interaction of the photons which make up the binding nuclear potential, effects which are predicted by QED. Indeed, these very effects and their influence on the wavefunctions of atomic systems are the main topic of this thesis.

The bound-state wavefunctions corresponding to the energies in Eq. (2.17) are of the form

$$\Phi_{n,\kappa,m_j}(r,\theta,\varphi) = \frac{1}{r}\begin{pmatrix} F_{n,\kappa}(r)\chi_{\kappa}^{m_j}(\theta,\varphi) \\ iG_{n,\kappa}(r)\chi_{-\kappa}^{m_j}(\theta,\varphi) \end{pmatrix}. \tag{2.18}$$

We will not be making use of the analytical solutions in this work, as we will modify the nuclear potential to account for the finite size of the nucleus and must then solve the Dirac equation numerically. The overall features of the solutions will however be the same, and just as an illustration we give here the radial components for the $1s$ state ($\kappa = -1$, $n = 1$) taken from [22]:

$$\begin{aligned} F_{1,-1}(r) &= \sqrt{\frac{1+\gamma}{2\Gamma(1+2\gamma)}}(2mZ\alpha)^{\gamma+\frac{1}{2}}r^{\gamma}e^{-mZ\alpha r} \\ G_{1,-1}(r) &= \left(\frac{\gamma-1}{Z\alpha}\right)F_{1,-1}(r) \end{aligned} \tag{2.19}$$

where $\gamma = \sqrt{1-(Z\alpha)^2}$. The exponential decay of this solution as $r \to \infty$ implies that the state is spatially *localized* — a typical feature of bound states.

For highly charged ions, the influence of the finite nuclear size upon observables is often significant, and this effect can be treated as a correction to the point-nucleus problem. Another approach, which we will adopt here, is to modify the nuclear potential $\phi(r)$ inside some nuclear boundary radius, typically taken as the root-mean-square charge-radius, to accomodate arbitrary (spherically symmetric) nuclear models. The finite-nucleus effect can then be incorporated into the wave-functions from the very beginning, but the solutions to 2.13 must in this case be found numerically.

3 Many-Body Perturbation Theory

The hydrogenic solutions (2.18) to the Dirac equation with a nuclear potential describe very well a single relativistic electron bound to an atomic nucleus. The description of multi-electron atoms and ions is more complicated since they contain, apart from the interaction of each individual electron with the atomic nucleus, also the interaction between the electrons. Even for two electrons interacting only via Coulombic repulsion, the problem is not exactly solvable and one must rely on approximation methods.

One such approximation method is many-body perturbation theory (MBPT) which will form the basis of our treatment of two-electron systems in later chapters. In this chapter we will give the main results from MBPT, largely following the exposition in Ref. [24].

3.1 Partitioning of the Hamiltonian

We are interested in the exact solutions to the full Hamiltonian H of a quantum system,

$$H|\Psi\rangle = E|\Psi\rangle. \tag{3.1}$$

Perturbation theory rests on a partitioning of H into a so-called *model Hamiltonian* H_0 and a perturbation V,

$$H = H_0 + V, \tag{3.2}$$

where it is assumed that the solutions to H_0,

$$H_0|\Psi^{(0)}\rangle = E^{(0)}|\Psi^{(0)}\rangle, \tag{3.3}$$

can be found either exactly or numerically to reasonable accuracy. Based on the solutions to H_0, approximations to the exact solutions can be constructed by making an expansion in terms of V. This expansion will be discussed further in Section 3.2, here we will focus on the model Hamiltonian and its solutions for few-electron ions.

For an atomic system consisting of N relativistic electrons bound by the nuclear electrostatic potential $V_{\text{nuc.}}(r)$, a reasonable choice[1] for the model Hamiltonian is a sum

$$H_0 = \sum_{j=1}^{N} \left[-i\boldsymbol{\alpha}\cdot\nabla_j - eV_{\text{nuc.}}(r_j) + \beta m\right] = \sum_{j=1}^{N} H_{\text{D}}(j) \tag{3.4}$$

of N single-electron Dirac Hamiltonians including the nuclear potential. This model Hamiltonian neglects the interaction between the electrons, and its solutions can be written as direct products

$$|\psi_i\psi_j...\rangle = |\psi_i\rangle \times |\psi_j\rangle \times ... \tag{3.5}$$

of N hydrogenic solutions $|\psi_i\rangle = |\psi_{n_i,\kappa_i,m_{j,i}}\rangle$ with energy ε_i:

$$H_{\text{D}}|\psi_i\rangle = \varepsilon_i|\psi_i\rangle. \tag{3.6}$$

[1] In some applications, especially for atoms or ions containing many electrons, it is common to include some mean-field potential for the interaction between the electrons in the model Hamiltonian as this typically leads to a faster convergence of the perturbation expansion.

The energy eigenvalue of the product-state (3.5) is given by the sum of single-electron energies $\varepsilon_i + \varepsilon_j + ...$

In order to satisfy the Pauli exclusion principle, the state of a many-electron system must be antisymmetric with respect to the interchange of any pair of electrons. This can be accomplished by the use of Slater determinants (given here in a spatial- and spin-coordinate representation):

$$\langle \mathbf{x}_1, ..., \mathbf{x}_N, \sigma_1, ..., \sigma_N | \Phi^{(0)} \rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1, \sigma_1) & \psi_1(\mathbf{x}_2, \sigma_2) & ... & \psi_1(\mathbf{x}_N, \sigma_N) \\ \psi_2(\mathbf{x}_1, \sigma_1) & \psi_2(\mathbf{x}_2, \sigma_2) & ... & \psi_2(\mathbf{x}_N, \sigma_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathbf{x}_1, \sigma_1) & \psi_N(\mathbf{x}_2, \sigma_2) & ... & \psi_N(\mathbf{x}_N, \sigma_N) \end{vmatrix} \tag{3.7}$$

In the case of a heliumlike (two-electron) system, which we will consider in later chapters, the model Hamiltonian (3.4) is a sum of two Dirac single-electron Hamiltonians, and the Slater determinant can be written as

$$\langle \mathbf{x}_1, \mathbf{x}_2, \sigma_1, \sigma_2 | \Phi^{(0)} \rangle = \frac{1}{\sqrt{2}} \left[\psi_1(\mathbf{x}_1, \sigma_1) \psi_2(\mathbf{x}_2, \sigma_2) - \psi_2(\mathbf{x}_1, \sigma_1) \psi_1(\mathbf{x}_2, \sigma_2) \right] \tag{3.8}$$

with energy $E^{(0)} = \varepsilon_1 + \varepsilon_2$.

Using a model Hamiltonian such as Eq. (3.4) the interaction between the electrons is treated as a perturbation, and approximating this interaction by a sum of instantaneous Coulomb repulsions we have

$$V = \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{e^2}{4\pi |\mathbf{x}_i - \mathbf{x}_j|} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{e^2}{4\pi |\mathbf{x}_i - \mathbf{x}_j|}. \tag{3.9}$$

In later chapters we will extend this treatment to also include the magnetic and retarded interactions as well as self-interactions from QED.

3.2 The Wave Operator and the Effective Hamiltonian

We are looking for an exact solution $|\Psi\rangle$ to the full Hamiltonian $H = H_0 + V$ and its corresponding exact energy E. For each exact solution there is a corresponding so-called *model state* $|\Psi^{(0)}\rangle$, with energy $E^{(0)}$, which is formed by solutions to the model Hamiltonian H_0. We will see below that we can construct an operator — the so-called *wave operator* — which transforms the model state into its corresponding exact state, but before that we need to introduce some concepts and definitions.

In general, the model state is formed by a linear combination of a set of Slater determinants $|\Phi^{(0)}\rangle$ (Eq. 3.7) — eigenstates to the model Hamiltonian (3.4). This set of Slater determinants spans the so-called *model space*. The model state is defined as the projection of the exact state onto the model space, which can be expressed using the projection operator P:

$$P|\Psi\rangle = |\Psi^{(0)}\rangle\langle\Psi^{(0)}|\Psi\rangle = |\Psi^{(0)}\rangle. \tag{3.10}$$

We will assume that the model state is normalized

$$\langle \Psi^{(0)} | \Psi^{(0)} \rangle = 1 \tag{3.11}$$

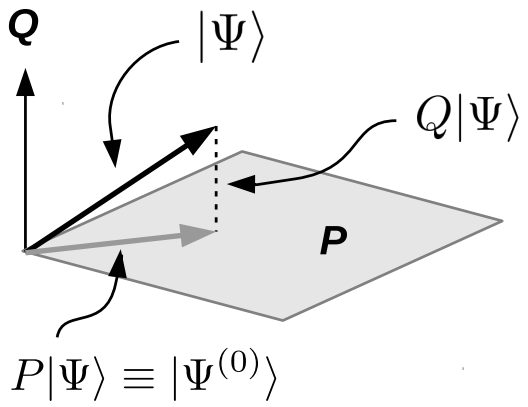


Figure 1: Illustration of the relation between the exact state (represented here by a black arrow) and the model state (represented by a grey arrow). The exact state lives in the full functional space, while the model state is the projection of the exact state onto the model space P. The difference between the model state and the exact state lives in the orthogonal space Q.

and Eq. (3.10) then implies that the exact state is *not* normalized. This is known as *intermediate normalization*.

The difference $|\Delta\Psi\rangle = |\Psi\rangle - |\Psi^{(0)}\rangle$ between the exact state and its model state lives in the complementary, or orthogonal, space with projection operator Q such that

$$P + Q = 1. \tag{3.12}$$

Obviously, we must have $PQ = QP = 0$. See Figure 1 for an illustration of the model space and the orthogonal space.

Since the model Hamiltonian H_0 is a Hermitean operator its eigenfunctions (3.5) span the full functional space, and the projection operators P and Q can therefore be represented as

$$\begin{aligned} P &= \sum_{|\psi_i\psi_j...\rangle \in P} |\psi_i\psi_j...\rangle\langle\psi_i\psi_j...| \equiv \sum_{\alpha\in P} |\alpha\rangle\langle\alpha|, \\ Q &= \sum_{|\psi_i\psi_j...\rangle \notin P} |\psi_i\psi_j...\rangle\langle\psi_i\psi_j...| \equiv \sum_{\beta\notin P} |\beta\rangle\langle\beta|, \end{aligned} \tag{3.13}$$

where we introduced a shorthand notation using the collective indices α, β, etc, which stand for the entire collection of single-electron states in a particular solution to H_0. From these relations it is evident that P and Q commute with H_0

$$[P, H_0] = [Q, H_0] = 0. \tag{3.14}$$

At this point we will introduce a simplifying assumption. In the applications to be considered in Part II we will only encounter model states which are made up of a single Slater determinant. Therefore we will already now specialize to the case of having a one-dimensional model space. It will then not be neccesary to distinguish between different parts of the model space having different energies, and this will simplify many of the expressions below. For the general case we refer the reader to Ref. [24].

We are now ready to discuss the wave operator. The definition of this operator (denoted by Ω) is that it generates the exact state from the corresponding model state:

$$|\Psi\rangle = \Omega|\Psi^{(0)}\rangle. \tag{3.15}$$

This equation serves merely as a formal definition of the wave operator and in order to use it we need an equation which we can solve in terms of the perturbation V. The derivation of such an equation is quite simple and proceeds as follows:

We start with the eigenvalue equation for the full Hamiltonian

$$H|\Psi\rangle = E|\Psi\rangle. \tag{3.16}$$

Using the partitioning of H into $H_0 + V$ we can write

$$(E - H_0)|\Psi\rangle = V|\Psi\rangle, \tag{3.17}$$

and projecting this equation onto the model space, using the commutation relation (3.14), we obtain

$$(E - H_0)|\Psi^{(0)}\rangle = PV|\Psi\rangle. \tag{3.18}$$

We now operate from the left with the wave operator, after first using the definition (3.15) to get rid of $|\Psi\rangle$ on the right-hand side,

$$(E\Omega - \Omega H_0)|\Psi^{(0)}\rangle = \Omega PV\Omega|\Psi^{(0)}\rangle. \tag{3.19}$$

The unknown energy E is eliminated by using Eq. (3.16)

$$((H_0 + V)\Omega - \Omega H_0)|\Psi^{(0)}\rangle = \Omega PV\Omega|\Psi^{(0)}\rangle \tag{3.20}$$

and by moving all the terms containing V to the right, we obtain

$$[\Omega, H_0]\, P = V\Omega P - \Omega PV\Omega P \tag{3.21}$$

which is known as the *generalized Bloch equation* [24]. Projection operators P occur on the right side of all the terms since this operator equation is only valid when acting upon model states.

The Bloch equation (3.21) can be used to generate a perturbation expansion of Ω in terms of V, but before we come to that, let us first note that once the wave operator has been obtained, we can immediately construct another operator — the so-called *effective Hamiltonian*

$$H_{\text{eff}} = PH\Omega P. \tag{3.22}$$

From the definition (3.15) of the wave operator and the eigenvalue relation (3.16) of H, it can be seen that the effective Hamiltonian generates the exact energy when operating on the model state:

$$H_{\text{eff}}|\Psi^{(0)}\rangle = E|\Psi^{(0)}\rangle. \tag{3.23}$$

Using the commutation relation (3.14) the effective Hamiltonian can be written as

$$H_{\text{eff}} = PH_0P + PV\Omega P \tag{3.24}$$

where the second term is known as the *effective interaction* $W_{\text{eff}} = PV\Omega P$ and it yields the energy shift when acting on the model state:

$$W_{\text{eff}}|\Psi^{(0)}\rangle = (E - E^{(0)})|\Psi^{(0)}\rangle \equiv \Delta E|\Psi^{(0)}\rangle. \tag{3.25}$$

The effective Hamiltonan and effective interaction will be used extensively in this work, although for QED we will find a generalized form for the effective interaction.

3.3 Perturbation Expansion of the Wave Operator

We come now to the perturbation expansion of Ω. Let us first consider what this operator must look like in zeroth order. From the definition of the model state in intermediate normalization, Eq. (3.10), we evidently must have

$$P\Omega P = P. \tag{3.26}$$

This means that Ω is of the form

$$\Omega = 1 + \chi \tag{3.27}$$

where χ is that part of Ω which generates the correction $|\Delta\Psi\rangle$ and resides completely in the orthogonal Q space:

$$P\chi P = 0. \tag{3.28}$$

Expanding the χ-part in terms of the number of interactions with the perturbation V we may write the wave operator as a sum

$$\Omega = 1 + \Omega^{(1)} + \Omega^{(2)} + ... \tag{3.29}$$

where $\Omega^{(n)}$ contains n interactions. Inserting this expansion into the Bloch equation (3.21) and equating terms of the same order in V, we find the first few terms to be

$$[\Omega^{(1)}, H_0]P = QVP, \tag{3.30}$$

$$[\Omega^{(2)}, H_0]P = QV\Omega^{(1)}P - \Omega^{(1)}PVP, \tag{3.31}$$

$$[\Omega^{(3)}, H_0]P = QV\Omega^{(2)}P - \Omega^{(2)}PVP - \Omega^{(1)}PV\Omega^{(1)}P. \tag{3.32}$$

The generalized form of the expansion is

$$[\Omega^{(n)}, H_0]P = QV\Omega^{(n-1)}P - \sum_{m=1}^{n-1} \Omega^{(n-m)}PV\Omega^{(m-1)}P. \tag{3.33}$$

Here appears, in the last term on the right, the operator $PV\Omega^{m-1}P$ which is the m-th order effective interaction

$$W_{\text{eff}}^{(m)} = PV\Omega^{(m-1)}P. \tag{3.34}$$

The general expansion can thus be written as

$$[\Omega^{(n)}, H_0]P = QV\Omega^{(n-1)}P - \sum_{m=1}^{n-1} \Omega^{(n-m)}W_{\text{eff}}^{m}. \tag{3.35}$$

The commutator on the left-hand side of these equations generates an energy-difference when operating on the solutions to the model Hamiltonian:

$$\langle\alpha|[\Omega^{(n)}, H_0]|\beta\rangle = (E_\beta^{(0)} - E_\alpha^{(0)})\langle\alpha|\Omega^{(n)}|\beta\rangle. \tag{3.36}$$

This energy-difference appears as a denominator when solving for $\Omega^{(n)}$ in matrix form, and by introducing the *resolvent*

$$\Gamma(\mathcal{E}) = \sum_\alpha \frac{|\alpha\rangle\langle\alpha|}{\mathcal{E} - E_\alpha^{(0)}} \tag{3.37}$$

as well as the *reduced resolvent*, which is restricted to the orthogonal space,

$$\Gamma_Q(\mathcal{E}) = Q\Gamma(\mathcal{E}) = \sum_{\alpha\notin P} \frac{|\alpha\rangle\langle\alpha|}{\mathcal{E} - E_\alpha^{(0)}} \tag{3.38}$$

the first few terms in the perturbation expansion of Ω can be written as

$$\Omega^{(1)}P = \Gamma_Q V P, \tag{3.39}$$

$$\begin{aligned}\Omega^{(2)}P &= \Gamma_Q V\Omega^{(1)}P - \Gamma_Q\Omega^{(1)}PVP \\ &= \Gamma_Q V\Omega^{(1)}P - \Gamma_Q\Omega^{(1)}W_{\text{eff}}^{(1)},\end{aligned} \tag{3.40}$$

$$\begin{aligned}\Omega^{(3)}P &= \Gamma_Q V\Omega^{(2)}P - \Gamma_Q\Omega^{(2)}PVP - \Gamma_Q\Omega^{(1)}PV\Omega^{(1)}P \\ &= \Gamma_Q V\Omega^{(2)}P - \Gamma_Q\Omega^{(2)}W_{\text{eff}}^{(1)} - \Gamma_Q\Omega^{(1)}W_{\text{eff}}^{(2)}.\end{aligned} \tag{3.41}$$

We remind ourselves that we are considering only one-dimensional model spaces here, and in this case the energy parameter $\mathcal{E}$ of the resolvent will, when acting with the wave operator upon the model state, be given by the model state energy $E^{(0)}$. In the general case one needs to differentiate between the different P's in these equations, and the energy parameter $\mathcal{E}$ of the resolvent then equals that of the nearest model state to the right.

The first terms on the right-hand sides of Eqs. (3.39 – 3.41) simply add an additional perturbation V, together with a resolvent (energy denominator), to the wave operator of previous order. The terms with a negative sign are known as *folded terms* (this nomenclature comes from the graphical treatment of the perturbation expansion in terms of Goldstone diagrams, where such terms are drawn in a "folded" or "backwards" way). These terms contain intermediate model states and can be expressed using the effective interaction. In order to interpret them we will look at their matrix representations.

The matrix element of the first-order correction $\Omega^{(1)}$ to the wave operator is simply

$$\langle\alpha|\Omega^{(1)}|\Psi^{(0)}\rangle = \langle\alpha|\Gamma_Q V|\Psi^{(0)}\rangle = \frac{\langle\alpha|V|\Psi^{(0)}\rangle}{E^{(0)} - E_\alpha^{(0)}},\ \alpha\notin P \tag{3.42}$$

(note here that the the resolvent $\Gamma_Q(\mathcal{E})$ "picks up" the energy of the model state). This yields the corresponding (well-known) correction to the wavefunction

$$|\Psi^{(1)}\rangle = \Omega^{(1)}|\Psi^{(0)}\rangle = \sum_\alpha |\alpha\rangle\langle\alpha|\Omega^{(1)}|\Psi^{(0)}\rangle = \sum_{\alpha\notin P} \frac{|\alpha\rangle\langle\alpha|V|\Psi^{(0)}\rangle}{E^{(0)} - E_\alpha^{(0)}}. \tag{3.43}$$

Proceeding in the same way, using our result for $\Omega^{(1)}$, we find for the matrix element of $\Omega^{(2)}$

$$\langle\alpha|\Omega^{(2)}|\Psi^{(0)}\rangle = \sum_{\gamma\notin P} \frac{\langle\alpha|V|\gamma\rangle\langle\gamma|V|\Psi^{(0)}\rangle}{(E^{(0)}-E_\alpha^{(0)})(E^{(0)}-E_\gamma^{(0)})} - \frac{\langle\alpha|V|\Psi^{(0)}\rangle\langle\Psi^{(0)}|V|\Psi^{(0)}\rangle}{(E^{(0)}-E_\alpha^{(0)})^2}. \quad (3.44)$$

The second term (the folded term) contains, via the presence of the intermediate model state, the expectation value of the first-order effective interaction

$$\Delta E^{(1)} = \langle\Psi^{(0)}|V|\Psi^{(0)}\rangle = \langle W_{\text{eff}}^{(1)}\rangle. \quad (3.45)$$

Furthermore, if we consider the matrix element of $\Omega^{(1)}$ (Eq. 3.42) as a function of the model-state energy, we can identify the squared energy-denominator in the folded term as the (negative of the) derivative of the denominator in (3.42). We can thus rewrite the folded term as

$$-\frac{\langle\alpha|V|\Psi^{(0)}\rangle\langle\Psi^{(0)}|V|\Psi^{(0)}\rangle}{(E^{(0)}-E_\alpha^{(0)})^2} = \left[\frac{\partial}{\partial\mathcal{E}}\langle\alpha|\Omega^{(1)}(\mathcal{E})|\Psi^{(0)}\rangle\right]_{\mathcal{E}=E^{(0)}} \times \Delta E^{(1)}. \quad (3.46)$$

This can be interpreted as the first term in a Taylor expansion which corrects the first-order matrix element (3.42) for the shift of the model-state energy due to the influence of the perturbation V. It can be shown that all of the folded terms in the perturbation expansion take the role of such corrections.

3.4 Iterative Expansion

As an alternative to the order-by-order expansion of Ω given in (3.35), one can take an iterative approach. To do this, we first rewrite the Bloch equation by using

$$V\Omega P = (P+Q)V\Omega P = PV\Omega P + QV\Omega P \quad (3.47)$$

as well as

$$-\Omega PV\Omega P = -(1+\chi)PV\Omega P = -PV\Omega P - \chi PV\Omega P. \quad (3.48)$$

The last relation can be found via the definition of χ in Eq. (3.27). We then obtain the equivalent form of the Bloch equation

$$[\Omega, H_0]\, P = QV\Omega P - \chi PV\Omega P. \quad (3.49)$$

Assuming that we know the wave operator to some approximation $\Omega^{(n)}$ (indeed, we can always start with $\Omega^{(0)}=1$ and $\chi^{(0)}=0$), the next improvement can be obtained by substituting $\Omega^{(n)}$ and $\chi^{(n)}$ in the right-hand side above:

$$\begin{aligned}\left[\Omega^{(n+1)}, H_0\right] P &= QV\Omega^{(n)}P - \chi^{(n)}PV\Omega^{(n)}P \\ &= QV\Omega^{(n)}P - \chi^{(n)}W_{\text{eff}}^{(n)}. \end{aligned} \quad (3.50)$$

This yields an alternative expansion of Ω, different from the order-by-order series, but which converges to the same result. In some applications the iterative approach is easier to implement, and we will find it useful when we treat electron correlation in later chapters.

3.5 No-Virtual-Pair Approximation

The (reduced) resolvent (3.38) that appears in the perturbation expansions of the wave operator introduces denominators in terms of the difference

$$E^{(0)} - E^{(0)}_{\alpha} \tag{3.51}$$

between the energy of the model-state and that of the intermediate state $|\alpha\rangle$. The intermediate states should be summed over the entire spectrum of eigenstates to the model Hamiltonian (restricted to the orthogonal Q space). If the model Hamiltonian is taken as a sum of single-electron Dirac Hamiltonians, these eigenstates will in general include combinations of single-electron states with negative and positive energy. For many-electron atoms, it can thus happen that the difference (3.51) vanishes, yielding a singular term in the expansion. In fact, infinitely many combinations of negative and positive states can be formed which have exactly the same energy as the model state. This troublesome fact is known as the *Brown-Ravenhall disease*, or sometimes as the *continuum dissolution* since it implies that the bound states are degenerate with a combination of negative and positive continuum states.

In order to remedy this problem, positive-energy projection operators Λ^+ are introduced to the Hamiltonian

$$H \to \Lambda^+ H \Lambda^+ \tag{3.52}$$

which effectively restricts all intermediate states to combinations of positive-energy electron states. This is known as the *no-virtual-pair approximation*.

In quantum field theory, the problem with vanishing energy-denominators does not appear since there the negative-energy electron states are redefined as positive-energy positron states which are included in a covariant manner into the perturbation expansion. This will be discussed further in the next chapter.

This concludes our discussion of the standard MBPT. The concepts introduced here will be very central to the developments later in this thesis.

4 Bound-State QED

We come now to the description of the theoretical framework of QED for bound states, which is the central theme of this thesis. Indeed, the ultimate goal of our efforts is to test this theory in the context of highly charged ions.

The theory of QED can be constructed by starting from the free-space Dirac equation (2.1). However, in quantum field theory it is not regarded as a single-particle wave equation in relativistic quantum mechanics, but rather as a classical field equation on the same conceptual level as Maxwell's equations for the electromagnetic field. The degrees of freedom of both of these fields are quantized in a scheme sometimes referred to as *second-quantization*, and this will give rise to the appearance of electrons, positrons, and photons.

We will here first recall the basics of Lagrangian field theory, before moving on to constructing the basic building blocks of bound-state QED. The presentation of the material in this chapter mostly follows Refs. [20], [25] and [26].

4.1 Lagrangian Field Theory

The principle of stationary action, $dS = 0$, is a general physical principle which can be used to obtain equations of motion for dynamical variables. In field theory, the dynamical variables are the field quantities ψ_i and their derivatives, while the spatial coordinates x, y, and z are demoted to the status of mere parameters together with the time coordinate t. The action S is given by a spacetime integral

$$S = \int d^4x \mathcal{L} \tag{4.1}$$

where the *Lagrangian density* $\mathcal{L}$ is a function of the fields ψ_i and their derivatives $\partial_\mu \psi_i$ on the spacetime manifold. The principle of stationary action can be shown to be equivalent to the *Euler-Lagrange equations* (see, e.g. [27]):

$$\frac{\partial \mathcal{L}}{\partial \psi_i} - \partial_\mu \left(\frac{\partial \mathcal{L}}{\partial(\partial_\mu \psi_i)} \right) = 0, \tag{4.2}$$

which are the equations of motion for the fields. In Lagrangian field theory, the fields ψ and their Hermitean conjugates $\psi^\dagger$ are treated as independent dynamical variables and each should satisfy Eq. (4.2).

The quantization of the fields is carried out in the so-called *canonical formalism*. This procedure relies upon the defintion of commutation relations between the dynamical variables and their conjugate momenta, which are treated as Heisenberg operators. The field conjugate to $\psi_i(x)$ is defined, in analogy with classical mechanics, as

$$\pi_i(x) = \frac{\partial \mathcal{L}}{\partial \dot{\psi}_i} \tag{4.3}$$

where the dot denotes a time-derivative.

The canonical quantization is achieved by imposing the (equal-time) commutation relations

$$\begin{aligned}
[\psi_i(\mathbf{x},t),\pi_j(\mathbf{y},t)] &= i\delta_{ij}\delta(\mathbf{x}-\mathbf{y}),\\
[\psi_i(\mathbf{x},t),\psi_j(\mathbf{y},t)] &= 0,\\
[\pi_i(\mathbf{x},t),\pi_j(\mathbf{y},t)] &= 0
\end{aligned} \tag{4.4}$$

upon the fields. These relations yield particles (field quanta) which obey Bose-Einstein statistics. For fermions, the commutators above should be replaced by anticommutators:

$$\begin{aligned}
\{\psi_i(\mathbf{x},t),\pi_j(\mathbf{y},t)\} &= i\delta_{ij}\delta(\mathbf{x}-\mathbf{y}),\\
\{\psi_i(\mathbf{x},t),\psi_j(\mathbf{y},t)\} &= 0,\\
\{\pi_i(\mathbf{x},t),\pi_j(\mathbf{y},t)\} &= 0.
\end{aligned} \tag{4.5}$$

Apart from being neccesary for the quantization of the theory, the conjugate fields (4.3) also allow for a definition of the field-theoretical Hamiltonian density

$$\mathcal{H}(x) = \sum_i \pi_i(x)\dot{\psi}_i(x) - \mathcal{L}(x) \tag{4.6}$$

such that the Hamiltonian is given by

$$H(t) = \int d^3\mathbf{x}\, \mathcal{H}(x). \tag{4.7}$$

We now turn to the Lagrangian density of QED.

4.2 The QED Lagrangian

The Lagrangian (from now on we will drop the term "density") which, via the principle of stationary action, gives rise to the free Dirac equation (2.1) is

$$\mathcal{L}_{\text{Dirac}} = \bar{\psi}(i\gamma^\mu\partial_\mu - m)\psi \tag{4.8}$$

where $\bar{\psi} = \psi^\dagger\gamma^0$ is the *Dirac adjoint* required to make $\bar{\psi}\psi$ a scalar under Lorentz transformations. Furthermore, the Dirac adjoint allows for the construction of a probability four-current

$$j^\mu = \bar{\psi}\gamma^\mu\psi \equiv (\rho,\mathbf{j}) \tag{4.9}$$

which satisfies a continuity equation

$$\partial_\mu j^\mu = \partial_t\rho + \nabla\cdot\mathbf{j} = 0. \tag{4.10}$$

The interaction with an electromagnetic field can be obtained by requiring that the Lagrangian should be invariant under the *local* phase transformation

$$\psi(x) \to \psi'(x) = e^{i\theta(x)}\psi(x). \tag{4.11}$$

In order for $\mathcal{L}$ to remain unaltered under this transformation, a counterterm $\gamma^\mu \partial_\mu \theta$ needs to be added which compensates for the derivative of the exponential:

$$\mathcal{L}_{\text{Dirac}} \to \mathcal{L}'_{\text{Dirac}} = \bar{\psi}(i\gamma^\mu \partial_\mu + \gamma^\mu \partial_\mu \theta - m)\psi = \mathcal{L}_{\text{Dirac}} + \bar{\psi}\gamma^\mu \partial_\mu \theta(x)\psi. \tag{4.12}$$

The counterterm has the form of an interaction term between the Dirac four-current $\bar{\psi}\gamma^\mu\psi$ and a Lorentz-covariant vector-valued field A^μ defined by

$$\partial_\mu \theta(x) = eA_\mu(x) \tag{4.13}$$

where e, the coupling constant, is equal to the magnitude of the electric charge of the electron. The interaction term $\mathcal{L}_{\text{int}}$ can thus be written as

$$\mathcal{L}_{\text{int}} = e\bar{\psi}\gamma^\mu A_\mu \psi, \tag{4.14}$$

and it is equivalent to the one obtained with the minimal substitution (Eq. 2.8).

A^μ can obviously be identified with the electromagnetic four-potential and by incorporating this field into the Lagrangian density we will also need to add a term which can give rise to the equations of motion for the free electromagnetic field, just as $\mathcal{L}_{\text{Dirac}}$ gives rise to the Dirac equation. The equations of motion we look for are of course Maxwell's equations in vacuum, which can be written in a manifestly covariant form as

$$\partial_\mu F^{\mu\nu} = 0 \tag{4.15}$$

$$\partial_\mu (\frac{1}{2}\epsilon^{\mu\nu\alpha\beta} F_{\alpha\beta}) = 0 \tag{4.16}$$

where $F^{\mu\nu}$ is the electromagnetic field-strength tensor

$$F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu \tag{4.17}$$

and $\epsilon^{\mu\nu\alpha\beta}$ is the totally antisymmetric tensor. The Lagrangian which gives rise to the Maxwell's equations via the stationary-action principle can then be written as [21]

$$\mathcal{L}_{\text{Maxwell}} = -\frac{1}{4} F_{\mu\nu} F^{\mu\nu}. \tag{4.18}$$

Finally, we can write down the total Lagrangian for QED, which contains the electron field, the electromagnetic field, and their interaction:

$$\begin{aligned} \mathcal{L}_{\text{QED}} &= \mathcal{L}_{\text{Dirac}} + \mathcal{L}_{\text{Maxwell}} + \mathcal{L}_{\text{int}} \\ &= \bar{\psi}(i\gamma^\mu \partial_\mu - m)\psi - \frac{1}{4} F_{\mu\nu} F^{\mu\nu} + e\bar{\psi}\gamma^\mu A_\mu \psi. \end{aligned} \tag{4.19}$$

This Lagrangian defines the particle content and interaction in QED, and in particular its corresponding Hamiltonian (Eq. 4.6) will be used in the construction of observable quantities.

4.3 The Quantized Dirac Field

In order to formulate QED for bound states we will separate out the part of A^μ which corresponds to the nuclear potential $A^\mu_{\rm nuc} = (V_{\rm nuc}, 0, 0, 0)$ and treat it as a classical field in the spirit of Section 2.1. This part will be included in the Dirac equation which defines the field of electrons and positrons. The remaining part of A^μ will be treated in the context of a quantized radiation field in the next section.

In terms of the solutions

$$\Psi_\alpha(x) = \Phi_\alpha(\mathbf{x})e^{-iE_\alpha t} \tag{4.20}$$

to the (single-particle) Dirac equation including the nuclear potential $A^\mu_{\rm nuc}$, the electron field ψ is expanded in the following way:

$$\begin{aligned}\psi(x) &= \sum_{E_\alpha>0} a_\alpha \Phi_\alpha(\mathbf{x})e^{-iE_\alpha t} + \sum_{E_\alpha<0} b_\alpha \Phi_\alpha(\mathbf{x})e^{-iE_\alpha t} \\ \psi^\dagger(x) &= \sum_{E_\alpha>0} a^\dagger_\alpha \Phi^\dagger_\alpha(\mathbf{x})e^{+iE_\alpha t} + \sum_{E_\alpha<0} b^\dagger_\alpha \Phi^\dagger_\alpha(\mathbf{x})e^{+iE_\alpha t}\end{aligned} \tag{4.21}$$

Here a generalized form of summation is implied, which includes an integration over the continuum of unbound states.

The quantization of this field is accomplished by imposing the anticommutation relations (4.5), which are equivalent to the following relations for the expansion coefficients:

$$\{a_\alpha, a^\dagger_\beta\} = \{b_\alpha, b^\dagger_\beta\} = \delta_{\alpha,\beta} \tag{4.22}$$

which then take the role of fermionic creation and annihilation operators. Specifically, $a^\dagger$ creates an electron of positive energy, while $b^\dagger$ creates an electron of negative energy. Similarly, a annihilates an electron of positive energy, while b annihilates an electron of negative energy.

The vacuum state of the electron field is defined as

$$a_\alpha|0\rangle = b^\dagger_\alpha|0\rangle = 0 \tag{4.23}$$

for all α. Thus, in the vacuum state, there are no positive-energy electrons to annihilate, but it is also not possible to create a negative-energy electron. The vacuum looks like it is "filled" with negative-energy electrons — this is the famous *Dirac sea* originally conceived by Dirac. Disregarding the possible difficulties of having a vacuum state which is of infinite negative charge, a negative-energy electron annihilated from this sea by the operator b would result in a state which appears to contain an "extra" elementary charge $+e$ relative to the vacuum state. In this way it can be loosely argued that the annihilation of a negative-energy electron is equivalent to the creation of a positron.

In a more rigorous manner, one starts by noting that the anticommutation relations (4.22) are symmetric with respect to interchange of b and $b^\dagger$. It can be shown (see e.g. [28]) that b actually plays the role of a *creation* operator for a *positive-energy* fermionic particle of charge $+e$ and mass m, while $b^\dagger$ acts as an annihilation operator for that same particle species (this interpretation does however come at the expense of having a Hamiltonian with an infinite expectation value). Thus, it

is more natural to interpret the field operator $\psi(x)$ in Eq. (4.21) as the annihilation (creation) of an electron (positron) at spacetime point x, while the operator $\psi^\dagger(x)$ should be interpreted as the creation (annihilation) of an electron (positron) at spacetime point x.

The Electron Propagator

The probability amplitude for propagation over a spacetime interval of a virtual particle (an electron or positron whose four-momentum is not neccesarily "on-shell", $p^2 \neq m^2$) of the Dirac field is described by the so-called fermionic *Feynman propagator*. This function, which is the Green's function for the Dirac equation, is defined as the vacuum expectation value

$$iS_{\mathrm{F}}(x,y) = \langle 0|T\left[\psi(x)\psi^\dagger(y)\right]|0\rangle, \tag{4.24}$$

where the *time-ordering operator* T has the property (with $x^0 \equiv t_x$ and $y^0 \equiv t_y$)

$$T\left[\psi(x)\psi^\dagger(y)\right] = \begin{cases} \psi(x)\psi^\dagger(y) & \text{if } t_x > t_y \\ -\psi^\dagger(y)\psi(x) & \text{if } t_x < t_y \end{cases} \tag{4.25}$$

Thus, there are two contributions to the vacuum expectation value (4.24): in the case that $t_x > t_y$, an electron is created at y and subsequently annihilated at x; this contribution describes electron propagation. Similarly, for $t_x < t_y$ a positron is created at x and is subsequently annihilated after propagating to y. The minus-sign for $t_x < t_y$ in the definition of T reflects the anticommutation property of the Dirac field.

From the expansion (4.21) of the Dirac field in terms of solutions including the nuclear potential, the propagator can be put into a form suited for practical applications. We first use the anticommutation relations of the creation and annihilation operators to obtain:

$$\begin{aligned} iS_{\mathrm{F}}(x,y) = \Theta(t_x - t_y) \sum_{E_\alpha > 0} \Phi_\alpha(\mathbf{x})\Phi_\alpha^\dagger(\mathbf{y})e^{-iE_\alpha(t_x - t_y)} \\ - \Theta(t_y - t_x) \sum_{E_\alpha < 0} \Phi_\alpha(\mathbf{x})\Phi_\alpha^\dagger(\mathbf{y})e^{-iE_\alpha(t_x - t_y)} \end{aligned} \tag{4.26}$$

Here, $\Theta(t)$ is the *Heaviside step function* which has the property

$$\Theta(t) = \begin{cases} 1 & \text{if } t > 0 \\ 0 & \text{if } t < 0 \end{cases} \tag{4.27}$$

The next step is to write the propagator in Eq. (4.26), with the help of Cauchy's integral formula, as a complex integral:

$$S_{\mathrm{F}}(x,y) = \int \frac{dz}{2\pi} e^{-iz(t_x - t_y)} \sum_\alpha \frac{\Phi_\alpha(\mathbf{x})\Phi_\alpha^\dagger(\mathbf{y})}{z - E_\alpha(1 - i\epsilon)} \tag{4.28}$$

This last relation contains the function

$$S_{\rm F}(\mathbf{x},\mathbf{y},z)=\sum_{\alpha}\frac{\Phi_{\alpha}(\mathbf{x})\Phi_{\alpha}^{\dagger}(\mathbf{y})}{z-E_{\alpha}(1-i\epsilon)} \tag{4.29}$$

which will turn out to be a basic ingredient in the construction of observables in bound state QED. Often we will refer to this function as "the electron propagator". The small imaginary part in the denominator serves to locate the poles properly in the complex plane — either above or below the real axis in accordance with the minus-sign in the second term of (4.26).

In free-electron QED, it is well-known that there are no contributions from fermions which propagate in a single closed loop, i.e., where the creation and annihilation takes place at the same spacetime point x. This is not the case for bound-state QED, since here the propagator is made up of an infinite series of interactions with the nuclear potential, and we are forced to define a propagator $S_{\rm F}(x,x)$. This is accomplished by defining the time ordering operator for equal times as

$$T\left[\psi(x)\psi^{\dagger}(x)\right]=\frac{1}{2}\left[\psi(x)\psi^{\dagger}(x)-\psi^{\dagger}(x)\psi(x)\right] \tag{4.30}$$

with the result

$$iS_{\rm F}(x,x)=\frac{1}{2}\sum_{\alpha}\mathrm{sgn}(E_{\alpha})\Phi_{\alpha}(\mathbf{x})\Phi_{\alpha}^{\dagger}(\mathbf{x}) \tag{4.31}$$

This *equal-coordinate* propagator will be used to describe the process of vacuum polarization in Section 4.6.3.

The complex variable z which appears in the propagator (4.29) plays the role of an energy parameter. Combinations of propagators that appear in the perturbation expansion of observables will, upon integration over these energy parameters, lead to expressions analogous to the resolvents $\Gamma(\mathcal{E})$ (Eq. 3.37) in standard many-body perturbation theory.

4.4 The Quantized Electromagnetic Field

It is quite complicated to formulate a rigorous theory of the quantized electromagnetic field which is explicitly covariant. The difficulties are due to the required symmetric treatment of all four spacetime indices on the four-potential A^{μ} in a covariant formulation, which introduces artificial degrees of freedom. We will here not go into the details of an explicitly covariant quantization, but simply give the most important results, mainly following Ref. [26].

Normally, explicit covariance is preferred in order to take advantage of the renormalization techniques developed to handle divergences in QED (see Appendix B). However, as Adkins has shown [29], the renormalization programme is perfectly valid also for the non-covariant Coulomb gauge, defined by the condition

$$\nabla\cdot\mathbf{A}=0. \tag{4.32}$$

Adkin's results were recently applied in Ref. [30] to compute the one-loop self-energy correction to the ground state energy of hydrogenic ions; the results are in perfect

agreement with those obtained in the covariant Feynman gauge (to be discussed below). We will be making extensive use of both these gauges in this work.

The Lagrangian given in Eq. (4.18) does not immediately lend itself to the canonical quantization procedure. From this Lagrangian the field conjugate to A^μ becomes

$$\pi^\mu(x) \equiv \frac{\partial \mathcal{L}}{\partial \dot{A}_\mu} = -F^{\mu 0}(x). \tag{4.33}$$

Due to the asymmetry of $F^{\mu\nu}$ (see Eq. 4.17), the time component π^0 is identically zero and therefore cannot form the basis of any meaningful commutation relation.

In order to circumvent this problem, one conventionally defines an alternative Lagrangian by adding a term $-\frac{\lambda}{2}(\partial_\nu A^\nu)^2$ in which λ is an arbitrary constant [26]. This leads to the conjugate field

$$\pi^\mu = -F^{\mu 0} - \lambda g^{0\mu}\partial_\nu A^\nu \tag{4.34}$$

whose time-component is non-vanishing and can be used to carry out the canonical quantization. The modified Lagrangian including the extra term implies a λ-dependent form of Maxwell's equations:

$$\partial_\nu \partial^\nu A^\mu - (1-\lambda)\partial^\mu(\partial_\nu A^\nu) = 0. \tag{4.35}$$

If we choose $\lambda = 1$ the Maxwell's equations take the particularly simple form

$$\partial_\nu \partial^\nu A^\mu = 0. \tag{4.36}$$

This choice of λ is usually referred to as the Feynman gauge (although strictly speaking it does not really correspond to a gauge fixing in the form of a gauge condition on A^μ — see Ref. [26] for details).

From Eq. (4.36), each component A^μ satisfies a relativistic wave-equation and can therefore be expanded in terms of plane waves:

$$A^\mu(x) = \int \frac{d^3\mathbf{k}}{(2\pi)^{3/2}} \sum_{r=0}^{3} \frac{1}{\sqrt{2k^0}} \epsilon_r^\mu(\mathbf{k}) \left[c_r(\mathbf{k}) e^{-ik\cdot x} + c_r^\dagger(\mathbf{k}) e^{ik\cdot x}\right] \tag{4.37}$$

where $k = (k^0, \mathbf{k})$ is the four-dimensional wave vector satisfying $k^0 = |\mathbf{k}|$. The index r labels the four polarization vectors ϵ_r^μ which we will here choose as follows: for $r = 0$ we take a unit vector in the time direction (scalar or timelike polarization), the unit vectors corresponding to $r = 1$ and $r = 2$ are chosen orthogonal to each other and to $\mathbf{k}$ (transverse polarization), and for $r = 3$ the vector is chosen to be $\mathbf{k}/|\mathbf{k}|$ (longitudinal polarization). In free space, only the transverse vectors correspond to physical solutions to Maxwell's equations, but in the interaction between charged particles all four polarizations contribute.

The quantization is accomplished via the commutation relations (4.4); the expansion coefficients in (4.37) are then promoted to creation and annihilation satisfying the following commutation relation:

$$[c_r(\mathbf{k}), c_s^\dagger(\mathbf{q})] = \zeta_r \delta_{r,s} \delta(\mathbf{k} - \mathbf{q}), \tag{4.38}$$

and this yields bosonic particles — the photons. The parameter ζ_r is equal to -1 for $r = 0$ and equal to 1 for $r = 1, 2, 3$. This has as a consequence that the norm of the scalar photon becomes negative. However, it can be shown that isolated, measurable states of negative norm are never formed in the theory, but rather linear combinations which always have positive norm [20, 28].

The quantization in Coulomb gauge affects only the spatial part $\mathbf{A}$ of the four-potential, and it can be shown that a modification of the commutation relation (4.4) is required in order to ensure that the gauge condition (4.32) is fulfilled. The correct (equal-time) commutation relation for the spatial components is most easily defined in terms of a Fourier transform as [26]

$$[A^i(\mathbf{x}), \pi^j(\mathbf{y})] = -i \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{y})} \left(\delta_{ij} - \frac{k^i k^j}{\mathbf{k}^2}\right). \tag{4.39}$$

The commutation relations for the expansion coefficients remain the same with this choice, and they still play the role of creation and annihilation operators. However, in the Coulomb gauge only the transverse polarization vectors ϵ_1^μ and ϵ_2^μ appear in the expansion (4.37).

The Photon Propagator

Similarly to the Dirac-field case, one can define a propagator for the electromagnetic field. This function describes the propagation of virtual photons (whose four-momentum is not neccesarily on-shell, $k^2 \neq 0$) in spacetime, and the exchange of virtual photons between charged particles provides a description of the electromagnetic interaction.

The Feynman photon propagator is defined, again involving the time-ordering operator T, as

$$iD_{\mathrm{F}}^{\mu\nu}(x-y) = \langle 0|T\left[A^\mu(x)A^\nu(y)\right]|0\rangle \tag{4.40}$$

and in Feynman gauge it has the form

$$D_{\mathrm{F}}^{\mu\nu}(x-y) = -g^{\mu\nu} \int \frac{d^4k}{(2\pi)^4} \frac{e^{-ik\cdot(x-y)}}{k^2 + i\delta}. \tag{4.41}$$

The integral over k^0 is performed over the entire real axis and the infinitesimal $\delta > 0$ defines the integration contour in the complex plane.

In order to be able to use the photon propagator together with our spectral representation of the electron propagator, Eq. (4.29), we will rewrite it by separating out the time dependence:

$$D_{\mathrm{F}}^{\mu\nu}(x-y) = \int \frac{dk^0}{2\pi} e^{-ik^0(t_x - t_y)} D_{\mathrm{F}}^{\mu\nu}(\mathbf{x}-\mathbf{y}, k^0), \tag{4.42}$$

where

$$D_{\mathrm{F}}^{\mu\nu}(\mathbf{x}-\mathbf{y}, z) = -g^{\mu\nu} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{e^{-i\mathbf{k}\cdot(\mathbf{x}-\mathbf{y})}}{z^2 - \mathbf{k}^2 + i\delta} \tag{4.43}$$

is analogous to the corresponding electron propagator in Eq. (4.29).

The choice of gauge for the electromagnetic field influences the form of the photon propagator. The general form can be written as

$$D_{\mathrm{F}}^{\mu\nu}(x-y) = \int \frac{d^4k}{(2\pi)^4} e^{-ik\cdot(x-y)} \frac{\tilde{D}^{\mu\nu}(k)}{k^2 + i\delta}. \tag{4.44}$$

We can then reproduce the Feynman-gauge expressions above by choosing $\tilde{D}^{\mu\nu}(k) = -g^{\mu\nu}$.

The photon propagator in Coulomb gauge can be obtained by instead choosing [26, 29]

$$\begin{aligned} \tilde{D}_{\mathrm{C}}^{00}(k) &= \frac{k^2}{\mathbf{k}^2} \\ \tilde{D}_{\mathrm{C}}^{ij}(k) &= \delta_{ij} - \frac{k^i k^j}{\mathbf{k}^2}. \end{aligned} \tag{4.45}$$

Here the scalar ($\mu = \nu = 0$) component gives an explicit description of the instantaneous Coulomb interaction, whereas in the Feynman gauge this interaction is described by a combination of scalar and longitudinal photons.

4.5 Perturbation Expansion of the Interaction

The Dirac and electromagnetic fields are coupled via the interaction term $\mathcal{L}_{\mathrm{int}}$ in the QED Lagrangian. So far we have treated a part of this interaction in a classical way — the interaction between the free Dirac field and the nuclear potential. The remaining part of the interaction which involves the quantized part of the electromagnetic field will be the topic of this section.

We will in this work treat the interaction in the recently developed covariant evolution-operator formalism which will be discussed in Chapter 5. Another approach which has been used extensively for bound-state QED applications in the past is the *S-matrix formalism*. The two approaches share many features and the covariant evolution-operator is most easily expressed in terms of the S-matrix. We will therefore here give a short review of the S-matrix approach. For further details we refer to Refs. [31] and [28].

We would also like to point out that a third approach to bound-state QED, developed by Shabaev and known as the *two-time Green's function method* (see [32] for details), has been applied with great success to various previously unsolved problems in recent years.

Up to now our formalism has been expressed in the *Heisenberg picture* of quantum mechanics, where the operators (the quantized fields) are time-dependent while the state vectors are constant. The time evolution is determined by the Hamiltonian (Eqs. 4.6 and 4.7), which can be separated as

$$H_{\mathrm{QED}}(t) = H_0(t) + H_{\mathrm{int}}(t). \tag{4.46}$$

In bound-state QED the zeroth-order Hamiltonian H_0 includes, apart from the Hamiltonians for the non-interacting Dirac and electromagnetic fields, also the the interaction of the electrons with the nuclear potential. The remaining part H_{int} of

the Hamiltonian is the space-integral of the corresponding *interaction Hamiltonian density*,

$$H_{\rm int}(t) = \int dV\ \mathcal{H}_{\rm int}(x) = \int dV\ \left[-e\bar{\psi}(x)\gamma^\mu A_\mu(x)\psi(x)\right]$$
$$= \int dV\ \left[-e\psi^\dagger(x)\alpha^\mu A_\mu(x)\psi(x)\right]. \tag{4.47}$$

The perturbation expansion of the interaction is most conveniently expressed in the so-called *interaction picture*, where the time-evolution of the operators is determined by the zeroth-order Hamiltonian H_0. The time-evolution of the state vectors is determined by the interaction Hamiltonian $H_{\rm int}$ and given by the equation

$$i\frac{d}{dt}|\Psi(t)\rangle = H_{\rm int}(t)|\Psi(t)\rangle. \tag{4.48}$$

This equation has a formal solution in terms of the integral equation

$$|\Psi(t)\rangle = |\Psi(t_0)\rangle - i\int_{t_0}^{t} dt_1\ H_{\rm int}(t_1)|\Psi(t_1)\rangle. \tag{4.49}$$

We define the time evolution operator $U(t,t_0)$ by

$$|\Psi(t)\rangle = U(t,t_0)|\Psi(t_0)\rangle \tag{4.50}$$

and from Eq. (4.49) we can find an iterative expansion of this operator:

$$U(t,t_0) = \sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\int_{t_0}^{t}dt_1\int_{t_0}^{t}dt_2\ldots\int_{t_0}^{t}dt_n\ T\left[H_{\rm int}(t_1)H_{\rm int}(t_2)\ldots H_{\rm int}(t_n)\right] \tag{4.51}$$

where the time-ordering operator arranges the interaction Hamiltonians so that later times appear to the left.

By using (4.47), and by extending the limits in the time integration to $\pm\infty$, we obtain the explicitly Lorentz-invariant result

$$U(\infty,-\infty) = \sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\int d^4x_1\int d^4x_2\ldots\int d^4x_n\ T\left[\mathcal{H}_{\rm int}(x_1)\mathcal{H}_{\rm int}(x_2)\ldots\mathcal{H}_{\rm int}(x_n)\right]. \tag{4.52}$$

This operator defines the S-matrix:

$$S_{fi} = \langle f|U(\infty,-\infty)|i\rangle \equiv \langle f|\hat{S}|i\rangle \tag{4.53}$$

which gives the amplitude for a system initially prepared in the state $|i\rangle$ at time $t=-\infty$ to be found in the state $|f\rangle$ at time $t=+\infty$, having been influenced by the interaction inbetween.

Obviously, the S-matrix is particularly well suited for the description of collision processes. In these cases, the states $|i\rangle$ and $|f\rangle$ can be considered as consisting of essentially non-interacting particles with well-defined momenta, and can be represented by solutions to the non-interacting equations of motion. For bound states the

situation is quite different. Here the interaction between the electrons is present all the time, and we cannot immediately express the S-matrix in terms of atomic solutions to a Hamiltonian which neglects the electron-electron interaction (the model Hamiltonian of Section 3.1).

In order to make use of the S-matrix formalism also in the bound-state case, the interaction Hamiltonian is modified by a damping factor:

$$H_{\text{int}}(t,\gamma) = e^{-\gamma|t|} H_{\text{int}}(t) \tag{4.54}$$

where $\gamma > 0$ is the *adiabatic parameter*. The damped interaction Hamiltonian yields, by substitution in (4.51), the corresponding adiabatic operators $U_\gamma(t,t_0)$ and $\hat{S}_\gamma = U_\gamma(\infty,-\infty)$. Furthermore, the damping allows us to express the S-matrix in terms of solutions $|\Psi^{(0)}\rangle$ which neglect the interaction (the model states). The $\gamma \to 0$ limit is taken at the end of the calculation to recover the full theory.

A typical goal in bound-state QED is to calculate the (real or complex) corrections to the energy of an atomic system. A level-shift formula in terms of the S-matrix was derived by Sucher [33], based on the work of Gell-Mann and Low [34], and reads

$$\Delta E = \lim_{\gamma\to 0} \frac{i\gamma e}{2} \frac{\frac{\partial}{\partial e}\langle\Psi^{(0)}|\hat{S}_\gamma|\Psi^{(0)}\rangle}{\langle\Psi^{(0)}|\hat{S}_\gamma|\Psi^{(0)}\rangle}. \tag{4.55}$$

This equation, together with the definition of the S-matrix (Eqs. 4.52 and 4.53), forms the basis of the S-matrix approach to bound-state QED.

Wick's Theorem

The iterative expansion of the evolution operator (4.52) and the construction of the corresponding S-matrix is greatly facilitated by *Wick's theorem* [35]. Using this theorem the time-ordered product of interaction Hamiltonians in (4.52) can be written in terms of the electron- and photon propagators introduced above as well as *normal-ordered* products of field operators.

A normal-ordered product of operators (denoted by N) is defined as one in which all creation operators stand to the left of the annihilation operators. We rewrite the time-ordered product as

$$T\left[AB\right] = N\left[AB\right] + \left(T\left[AB\right] - N\left[AB\right]\right) \tag{4.56}$$

The quantity in parentheses is known as the *contraction* of the operators A and B

$$\overbracket{AB} = T\left[AB\right] - N\left[AB\right] \tag{4.57}$$

and it can be shown (see, e.g. Ref. [20]) that the only non-vanishing contractions are between field-operators of the same kind, and that these contractions are identical to the propagators of the fields contained in the theory. Specifically for the case of bound-state QED we have:

$$\overbracket{\psi(x)\psi^\dagger}(y) = -\overbracket{\psi^\dagger(y)\psi}(x) = iS_{\text{F}}(x,y) \tag{4.58}$$

$$\overbracket{A^\mu(x)A^\nu}(y) = iD_{\text{F}}^{\mu\nu}(x-y) \tag{4.59}$$

Wick's theorem generalizes Eq. (4.56) to

$$T[ABC...] = N[ABC...] + N[\overbracket{A}BC...] + N[A\overbracket{B}C...] + N[\overbracket{AB}C...] + N[A\overbracket{BC}...] + N[\overbracket{ABC}...] + ... \tag{4.60}$$

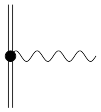
Wick's theorem means for the S-matrix the following: in the expansion of S_{fi}, only those terms which involve precisely the correct uncontracted annihilation and creation operators to absorb the particles present in the initial state $|i\rangle$ and create the particles present in the final state $|f\rangle$ will contribute. In general these terms will also contain factors of contracted operators which are equal to the propagators of the theory.

Feynman Diagrams

Upon using Wick's theorem, each term in the perturbation expansion of the S-matrix can be represented by a so-called *Feynman diagram*, in which there is a direct correspondence between the graphical elements in the diagram and the factors in the so-called *Feynman amplitude* $\mathcal{M}$, which is related to the S-matrix element as

$$\langle f|\hat{S}|i\rangle = 2\pi\delta(E_i - E_f)\langle f|\mathcal{M}|i\rangle. \tag{4.61}$$

A Feynman diagram in bound-state QED consists of the following parts:

- For each incoming electron $\Phi(\mathbf{x})$, 
- For each outgoing electron $\Phi^\dagger(\mathbf{x})$, 
- For each interaction vertex $ie\alpha^\mu$, 
- For each electron propagator $iS_{\mathrm{F}}(\mathbf{x}, \mathbf{y}, z)$,
- For each photon propagator $iD^{\mathrm{F}}_{\mu\nu}(\mathbf{x} - \mathbf{y}, z)$,
- For each interaction with an external potential $A^{\mathrm{ext}}_\mu(\mathbf{x})$,

In order to obtain a unique relation between the diagrams and the corresponding algebraic expression for the Feynman amplitude there are additional rules, e.g. concerning the treatment of energy parameters at vertices. We will not go into these details here as we will mainly make use of Feynman diagrams for the purpose of visualization.

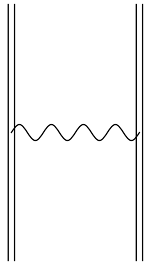


Figure 2: The Feynman diagram for single photon exchange.

4.6 Equivalent Potentials

The QED corrections to observables we will consider in this thesis are all due to processes involving a single full photon propagator, and we will here give the expressions for these processes in the S-matrix formalism. The corresponding energy-shifts obtained with Sucher's level shift formula imply that we can consider these processes in terms of their *equivalent perturbing potentials* which we will use when we include the QED-effects into the wavefunction.

4.6.1 Single Photon Exchange

The $n = 2$ term in (4.52) contains two interaction Hamiltonians, and depending on how the field operators are contracted when using Wick's theorem this term will correspond to different processes. Contracting only the photon field operators yields a (gauge-dependent) photon propagator times four uncontracted Dirac field operators. This will describe single-photon exchange (SPE) between two electrons (see Figure 2). The corresponding S-matrix element is

$$\begin{aligned} S_{fi,\gamma}^{(2),\mathrm{SPE}} =& \frac{(ie)^2}{2} \int \frac{dz}{2\pi} \int d^4x \int d^4y \; \Phi_c^\dagger(\mathbf{x}) \alpha_\mu \Phi_a(\mathbf{x}) i D_{\mathrm{F}}^{\mu\nu}(\mathbf{x}-\mathbf{y}, z) \Phi_d^\dagger(\mathbf{y}) \alpha_\nu \Phi_b(\mathbf{y}) \\ & \times e^{-\gamma(|t_x|+|t_y|)} e^{-it_x(E_a - E_c + z)} e^{-it_y(E_b - E_d - z)}. \end{aligned} \tag{4.62}$$

Here we have assumed that the initial state consists of two electrons in energy-eigenstates described by Φ_a and Φ_b, and the final state contains the two electrons in energy-eigenstates Φ_c and Φ_d. The energy parameter z enters through the photon propagator (given in Feynman gauge in Eq. 4.43).

In order to perform the time-integrations, we introduce the Δ_γ function defined by

$$\Delta_\gamma(x) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{-ixt} e^{-\gamma|t|} = \frac{1}{\pi} \frac{\gamma}{x^2 + \gamma^2}, \tag{4.63}$$

which has the following properties

$$\lim_{\gamma\to 0}\Delta_\gamma(x) = \delta(x) \tag{4.64}$$

$$\lim_{\gamma\to 0}\pi\gamma\Delta_\gamma(x) = \delta_{x,0} \tag{4.65}$$

$$\lim_{\gamma\to 0}\Delta_\gamma(x-a)f(x) = \lim_{\gamma\to 0}\Delta_\gamma(x-a)f(a) \tag{4.66}$$

$$\int_{-\infty}^{\infty} dx\ \Delta_{n\gamma}(x-a)\Delta_{m\gamma}(x-b) = \Delta_{(n+m)\gamma}(a-b) \tag{4.67}$$

for integer n and m.

We can then write the result from the time-integrations as

$$\begin{aligned} S_{fi,\gamma}^{(2),\mathrm{SPE}} =& \frac{(ie)^2}{2}\int\frac{dz}{2\pi}\int d^3\mathbf{x}\int d^3\mathbf{y}\ \Phi_c^\dagger(\mathbf{x})\alpha_\mu\Phi_a(\mathbf{x})iD_{\mathrm{F}}^{\mu\nu}(\mathbf{x}-\mathbf{y},z)\Phi_d^\dagger(\mathbf{y})\alpha_\nu\Phi_b(\mathbf{y}) \\ &\times(2\pi)^2\Delta_\gamma(E_a-E_c+z)\Delta_\gamma(E_b-E_d-z). \end{aligned} \tag{4.68}$$

Using the properties of the Δ_γ function, we can perform the z integration and obtain

$$\begin{aligned} S_{fi,\gamma}^{(2),\mathrm{SPE}} =& \frac{(ie)^2}{2}\int d^3\mathbf{x}\int d^3\mathbf{y}\ \Phi_c^\dagger(\mathbf{x})\alpha_\mu\Phi_a(\mathbf{x})iD_{\mathrm{F}}^{\mu\nu}(\mathbf{x}-\mathbf{y},E_c-E_a)\Phi_d^\dagger(\mathbf{y})\alpha_\nu\Phi_b(\mathbf{y}) \\ &\times 2\pi\Delta_{2\gamma}(E_c+E_d-E_a-E_b) \end{aligned} \tag{4.69}$$

where we note that the energy-parameter of the photon propagator has changed so that energy is conserved in the photon emission.

Finally, inserting this expression into the Sucher level shift formula (Eq. 4.55) and taking the $\gamma\to 0$ limit we obtain, using (4.65), the energy shift due to single-photon exchange

$$\Delta E_{\mathrm{SPE}} = \delta_{E_{\mathrm{in}},E_{\mathrm{out}}}e^2\int d^3\mathbf{x}\int d^3\mathbf{y}\ \Phi_c^\dagger(\mathbf{x})\alpha_\mu\Phi_a(\mathbf{x})D_{\mathrm{F}}^{\mu\nu}(\mathbf{x}-\mathbf{y},E_c-E_a)\Phi_d^\dagger(\mathbf{y})\alpha_\nu\Phi_b(\mathbf{y}), \tag{4.70}$$

where $E_{\mathrm{in}} = E_a + E_b$ and $E_{\mathrm{out}} = E_c + E_d$.

This result can be written as

$$\Delta E_{\mathrm{SPE}} = \delta_{E_{\mathrm{in}},E_{\mathrm{out}}}\langle cd|I(E_c-E_a)|ab\rangle \tag{4.71}$$

where

$$I(z) \equiv I(\mathbf{x}-\mathbf{y},z) = e^2\alpha_\mu\alpha_\nu D_{\mathrm{F}}^{\mu\nu}(\mathbf{x}-\mathbf{y},z) \tag{4.72}$$

plays the role of an energy-dependent equivalent perturbing potential. This equivalent potential is gauge-dependent and can for general (positive-energy) states be written as [16, 36]

$$\begin{aligned} &\langle rs|I(z)|tu\rangle \equiv \langle rs|V_{\mathrm{SPE}}(\mathcal{E})|tu\rangle \\ &= \langle rs|\int_0^\infty d|\mathbf{k}|f(|\mathbf{k}|)\left[\frac{1}{\mathcal{E}-E_u-E_r-(|\mathbf{k}|-i\delta)}+\frac{1}{\mathcal{E}-E_t-E_s-(|\mathbf{k}|-i\delta)}\right]|tu\rangle \end{aligned} \tag{4.73}$$

where $f(|\mathbf{k}|)$ is a gauge-dependent function. The relation (4.73) holds for the entire interaction in Feynman gauge and for the transverse part in Coulomb gauge.

The equivalent potential V_{SPE} will be used to include photon exchanges in a perturbation expansion of the atomic wavefunction in later chapters, the parameter $\mathcal{E}$ will then be equal to the model state energy.

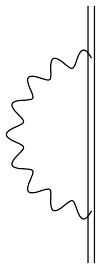


Figure 3: The Feynman diagram for the (one-loop) single-electron self-energy.

4.6.2 Electron Self-Energy

If (apart from the photon field operators) we also contract two electron field operators in the $n = 2$ term of the S-matrix, we find an expression for the single-electron self-energy process (Figure 3):

$$S_{fi,\gamma}^{(2),\mathrm{SE}} = \frac{(ie)^2}{2} \int \frac{dz}{2\pi} \int \frac{d\omega}{2\pi} \int d^4x \int d^4y \; \Phi_b^\dagger(\mathbf{x}) \alpha_\mu \alpha_\nu i D_{\mathrm{F}}^{\mu\nu}(\mathbf{x}-\mathbf{y}, z) i S_{\mathrm{F}}(\mathbf{x}, \mathbf{y}, \omega) \Phi_a(\mathbf{y}) \\ \times e^{-\gamma(|t_x|+|t_y|)} e^{-it_x(z+\omega-E_b)} e^{-it_y(E_a-z-\omega)}. \tag{4.74}$$

Proceeding as in the case for single photon exchange, the integrations over t_x, t_y and ω give

$$S_{fi,\gamma}^{(2),\mathrm{SE}} = 2\pi \Delta_{2\gamma}(E_a - E_b) \int \frac{dz}{2\pi} \int d^3\mathbf{x} \int d^3\mathbf{y} \\ \times \Phi_b^\dagger(\mathbf{x}) I(\mathbf{x}-\mathbf{y}, z) S_{\mathrm{F}}(\mathbf{x}, \mathbf{y}, E_a - z) \Phi_a(\mathbf{y}). \tag{4.75}$$

Inserting this result into the Sucher level shift formula, taking the $\gamma \to 0$ limit, yields the energy shift due to the electron self energy

$$\Delta E_{\mathrm{SE}} = \delta_{E_a, E_b} \langle b | \Sigma(E_a) | a \rangle \tag{4.76}$$

where

$$\Sigma(\omega) = i \int \frac{dz}{2\pi} I(\mathbf{x}-\mathbf{y}, z) S_{\mathrm{F}}(\mathbf{x}, \mathbf{y}, \omega - z) \tag{4.77}$$

is the (gauge-dependent) electron self-energy operator.

As it stands, the self-energy operator is divergent due to a non-convergent integral over the four-momentum of the photon. This well-known problem is related to the definition of the electron mass appearing in the QED Lagrangian. It turns out that the divergent part of the self-energy operator acts as a correction to the observed mass of the electron. This divergence can be removed from all observable quantities if we re-interpret the mass appearing in the Lagrangian as the mass m_0 of an ideal, non-interacting electron (which consequently does not experience the self-energy process). We can reformulate the theory in terms of the experimentally observed mass m of the physical, interacting electron if we add a counterterm $\bar{\psi}\psi\delta m$ to the Lagrangian which compensates for this reformulation. By defining the physical electron mass to include the (infinite) correction from the self-energy process, it

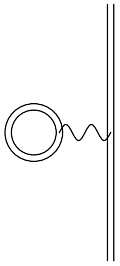


Figure 4: The Feynman diagram for the (one-loop) single-electron vacuum polarization.

can be shown that observable quantities will always be finite if the self-energy operator is consistently considered together with the mass counterterm. This procedure, known as *renormalization*, is described in more detail in Refs. [20, 28]. It should be pointed out that renormalization would be neccessary even if the integral in the self-energy operator had been finite, since we have no access to the mass m_0 of the non-interacting electron and are thus forced to formulate the theory in terms of the observable mass m which includes the self-energy correction.

After mass renormalization, the self-energy operator becomes

$$\Sigma(\omega) \to \Sigma(\omega) - \gamma^0 \delta m \equiv \Sigma_{\rm ren}(\omega) \tag{4.78}$$

where $\Sigma_{\rm ren}$ is known as the *renormalized* self-energy operator. This operator is the energy-dependent equivalent potential for the self-energy process.

4.6.3 Vacuum Polarization

The final single-photon QED process we will consider here is the result of contracting, apart from the photon fields, two electron-field operators from the *same* interaction Hamiltonian (evaluated at the same spacetime point), which corresponds to the so-called *vacuum polarization* (see Figure 4). This contraction yields a closed fermion loop, and if we explicitly write out the spinor components in the interaction Hamiltonian we find that the contraction can be written in terms of the trace of the matrix

$$\overbrace{\psi_a^\dagger(x)\alpha^\mu_{ab}A_\mu(x)\psi}_b(x) = {\rm Tr}[\overbrace{\psi^\dagger(x)\alpha^\mu A_\mu(x)\psi}(x)]. \tag{4.79}$$

Performing the contraction yields a factor $-iS_{\rm F}(x,x)$ and the S-matrix element becomes

$$\begin{aligned} S^{(2),{\rm VP}}_{fi,\gamma} =& \frac{(ie)^2}{2}\int\frac{dz}{2\pi}\int\frac{d\omega}{2\pi}\int d^4x\int d^4y\;\Phi_b^\dagger(\mathbf{x})\alpha_\mu\Phi_a(\mathbf{x})iD_{\rm F}^{\mu\nu}(\mathbf{x}-\mathbf{y},z) \\ &\times{\rm Tr}\left[-iS_{\rm F}(\mathbf{y},\mathbf{y},\omega)\alpha_\nu\right]e^{-\gamma(|t_x|+|t_y|)}e^{-it_x(E_a-E_b-z)}e^{-it_y(\omega-\omega+z)}. \end{aligned} \tag{4.80}$$

Proceeding with the integrations as in the previous cases, this gives the level shift due to vacuum polarization:

$$\Delta E_{\rm VP} = -\delta_{E_a,E_b}\langle b|U_{\rm VP}|a\rangle \tag{4.81}$$

where the vacuum polarization potential is formally given by

$$U_{\mathrm{VP}}(\mathbf{x}) = -ie^2 \int d^3\mathbf{y} \int \frac{dz}{2\pi} \alpha_\mu D_{\mathrm{F}}^{\mu\nu}(\mathbf{x}-\mathbf{y},0) \mathrm{Tr}\left[\alpha_\nu S_{\mathrm{F}}(\mathbf{y},\mathbf{y},z)\right]. \tag{4.82}$$

The vacuum polarization potential is, in constrast to the self-energy and single photon exchange, local (depends only on $\mathbf{x}$) as well as energy- and gauge-independent. Furthermore, it can be shown that only the $\nu = 0$ components give non-vanishing contributions to the matrix elements of this potential.

Similarly to the self-energy operator, the vacuum polarization potential is divergent as is stands. By a renormalization of the charge of the electron, the correct finite potential can be derived (see e.g. [20]). We will denote the renormalized vacuum polarization potential by $U_{\mathrm{VP}}^{\mathrm{ren}}$, and it will be discussed more closely when we consider the numerical implementation of this potential in Section 6.4.5.

This concludes our discussion of the standard formalism of bound-state QED. We will now move on to describe how the building blocks constructed here can be used in an extension of the standard formalism which will allow us to consider corrections not only to the bound-state energies, but also to the wavefunctions.

5 The Green's Operator: A Wave Operator for QED

The aim of this chapter is to construct the so-called *Green's operator* which is the central object in the covariant evolution-operator formalism, and which will turn out to act as a wave operator for QED. This will allow us to include the effects of QED directly into the atomic wavefunction, and from this we can compute observable quantities. The main utility of this formalism consists in two properties: 1) it is relatively straightforward, in contrast to the S-matrix formalism, to obtain expressions for the so-called *model-space contributions* which are finite remainders from singular terms involving intermediate model-space states in the perturbation expansion, and 2) it is possible to obtain an iterative perturbation expansion of the Green's operator which can be solved to all orders using present-day numerical techniques (if certain restrictions are made on how intermediate negative-energy states are included). The iterative expansion of the Green's operator will be discussed in Part II when we apply the formalism to compute the combined effect of correlation and QED in heliumlike systems.

The presentation in this chapter mostly follows Ref. [16]. The derivation of some of the results given here are rather lengthy, and for brevity we will quote some of them without proof. For further details, we refer the reader to Refs. [13, 14, 16, 17].

5.1 The Covariant Evolution-Operator

The operator we are looking to construct — the Green's operator — is formally defined in terms of another operator, known as the *covariant evolution-operator*, which was introduced by Lindgren *et al.* in the beginning of this century [13,36]. It is therefore neccesary to define this operator in this section.

The covariant evolution-operator $U_{\text{cov}}(t, t_0)$ is a relativistic time-evolution operator for finite initial and final times t_0 and t. However, the interactions which are involved in the perturbation expansion of this operator are not restricted to this time interval, but may occur anywhere between $t = -\infty$ and $t = +\infty$. The finite final and inital times has the consequence that energy is not neccesarily conserved, and matrix elements of this operator which are not diagonal in energy can be constructed, while the unrestricted internal times allow for the complete inclusion of intermediate positron states in the perturbation expansion.

The covariant evolution-operator is in the single-electron case defined as

$$U^1_{\text{cov}}(t, t_0) = \int d^3\mathbf{x} \int d^3\mathbf{x}_0 \; \psi^\dagger(x) \langle 0 | T \left[\psi(x) U^1(\infty, -\infty) \psi^\dagger(x_0) \right] | 0 \rangle \psi(x_0) \qquad (5.1)$$

where $U^1(\infty, -\infty)$ is that part of the standard evolution operator (4.52) which connects a single incoming electron to a single outgoing electron — i.e. that part which, after performing the contractions in Wick's theorem, contains a single uncontracted annihilation operator for the incoming electron as well as a single uncontracted creation operator for the outgoing electron.

Let us examine the parts of the right-hand side of (5.1). The innermost part is

a time-ordered product

$$T\left[\psi(x)U^1(\infty,-\infty)\psi^\dagger(x_0)\right] \tag{5.2}$$

of three operators — an electron creation operator $\psi^\dagger(x_0)$, the time-evolution operator $U^1(\infty,-\infty)$ containing two uncontracted electron operators, and finally an electron annihilation operator $\psi(x)$. Again, via Wick's theorem, this product can be written as a sum of normal-ordered terms involving all possible contractions. Only the fully-contracted term, in which the creation operator $\psi^\dagger(x_0)$ is contracted with the annihilation operator in $U^1(\infty,-\infty)$ and the annihilation operator $\psi(x)$ is contracted with the creation operator in $U^1(\infty,-\infty)$, will contribute to the vacuum expectation value.

The vacuum expectation value in Eq. (5.1) is a function of the two spacetime coordinates x_0 and x. Due to the contractions just described, it contains one incoming and one outgoing electron propagator:

$$\langle 0|T\left[\psi(x)U^1(\infty,-\infty)\psi^\dagger(x_0)\right]|0\rangle = \int d^4y_1 \int d^4y_2\; iS_{\rm F}(x,y_1)f(y_1,y_2)iS_{\rm F}(y_2,x_0) \tag{5.3}$$

where $f(y_1,y_2)$ contains no uncontracted field operators. The vacuum expectation value (5.3) is Lorentz covariant and describes electron propagation from x_0 to x under the influence of the interaction Hamiltonian.

Connected to the vacuum expectation value are electron creation and annihilation operators, evaluated at the same spacetime coordinates as the expectation value (5.3), with integration over the spatial part. An initial electron state will thus be annihilated at time t_0 by the rightmost $\psi(x_0)$ in Eq. (5.1), reappear, evolve, and annihilate under the influence of the interaction according to the vacuum expectation value (5.3), and finally appear again at time t due to the leftmost $\psi^\dagger(x)$. This completes the time-evolution from t_0 to t.

In analogy with the single-electron case, the covariant evolution operator for two electrons is defined as

$$\begin{aligned} U^2_{\rm cov}(t,t',t_0,t_0') = \int d^3\mathbf{x}\int d^3\mathbf{x}'\int d^3\mathbf{x}_0\int d^3\mathbf{x}_0'\; \psi^\dagger(x)\psi^\dagger(x')\times \\ \langle 0|T\left[\psi(x)\psi(x')U^2(\infty,-\infty)\psi^\dagger(x_0)\psi^\dagger(x_0')\right]|0\rangle\times \\ \psi(x_0)\psi(x_0'), \end{aligned} \tag{5.4}$$

the difference being that we retain uncontracted electron field operators for two incoming and outgoing electrons in $U(\infty,-\infty)$.

In words, we can give the following "recipe" for the construction of the covariant evolution operator for n electrons:

1. Construct the standard evolution operator to the desired order of approximation according to Eq. (4.51), retaining n incoming and n outgoing uncontracted electron field operators whose coordinates are not integrated over.

2. Replace each uncontracted creation operator with an electron propagator times a creation operator, $\psi^\dagger(y) \to \psi^\dagger(x)iS_{\rm F}(x,y)$, and correspondingly for each uncontracted annihilation operator, $\psi(y') \to iS_{\rm F}(y',x_0)\psi(x_0)$.

3. Integrate over the internal spacetime coordinates, keeping the coordinates of the outermost field operators fixed.

4. Integrate over the spatial coordinates of the outermost field operators, keeping the time coordinates fixed.

In the formalism that follows, we will mainly make use of the covariant evolution-operator in the limit that all initial times tend to $-\infty$. Furthermore, in the multi-electron case we will employ the *equal-time approximation* in which all final times are set equal.

Ultimately, the justification for the definitions of the covariant evolution-operator introduced in this section is that they can be used to reproduce established results in bound-state QED, while also being able to go beyond the traditional S-matrix approach due to the relaxation of the energy-conservation condition.

Matrix Elements of the Covariant Evolution-Operator

We will now consider some matrix elements of the covariant evolution-operator. In the limit that the initial time t_0 tends to $-\infty$, it can be shown that

$$\int d^3\mathbf{x}_0 \; iS_{\mathrm{F}}(x, x_0)\psi(x_0) \to \psi(x) \tag{5.5}$$

and this will allow us to disregard the incoming propagators in the definition of the covariant evolution-operator, expressing it directly in terms of an incoming model state.

Consider first the single-electron case, and the matrix element of the covariant evolution-operator for the interaction with a time-independent external potential given by A_μ^{ext}. From the interaction Hamiltonian (4.47) and the expansion (4.52) we obtain, using the definition (5.1),

$$U_{\mathrm{cov},\gamma}^{\mathrm{ext}}(t, -\infty) = -e \int d^3\mathbf{x} \; \psi^\dagger(x) \int d^4y \; iS_{\mathrm{F}}(x, y)\alpha^\mu A_\mu^{\mathrm{ext}}(y)\psi(y)e^{-\gamma|t_y|}. \tag{5.6}$$

The matrix element of this operator with respect to the incoming state $|a\rangle$ and outgoing state $|r\rangle$ can in the limit $\gamma \to 0$ be shown to be [16]

$$\langle r|U_{\mathrm{cov}}^{\mathrm{ext}}(t, -\infty)|a\rangle = \frac{e^{-it(E_a - E_r)}}{E_a - E_r}\langle r|V_{\mathrm{ext}}|a\rangle \tag{5.7}$$

where the matrix element of the external potential is given by

$$\langle r|V_{\mathrm{ext}}|a\rangle = -e \int d^3\mathbf{x} \; \Phi_r^\dagger(\mathbf{x})\alpha^\mu A_\mu^{\mathrm{ext}}(\mathbf{x})\Phi_a(\mathbf{x}). \tag{5.8}$$

Similarly, it can be shown [16] that the two-electron matrix elements of the covariant evolution-operator for single photon exchange are, in the limit $\gamma \to 0$,

$$\langle rs|U_{\mathrm{cov}}^{\mathrm{SPE}}(t, -\infty)|ab\rangle = \frac{e^{-it(E_a + E_b - E_r - E_s)}}{E_a + E_b - E_r - E_s}\langle rs|V_{\mathrm{SPE}}|ab\rangle \tag{5.9}$$

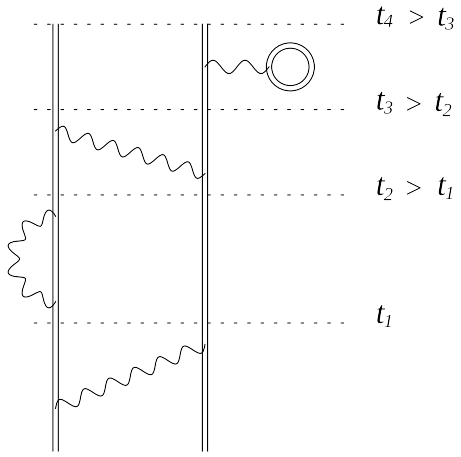


Figure 5: A ladder-type term the expansion of the covariant evolution-operator. Perturbations appearing in a certain time order can be written as products of lower-order evolution operators if only positive-energy (electron) intermediate states are present at the different times indicated in the figure.

which contains the matrix element of the potential for single photon exchange (Eq. 4.73).

In general, the matrix elements of the covariant evolution-operator for a certain process can be obtained from the corresponding equivalent potential, with extra energy denominators due to the outgoing electron propagators, as well as an overall factor of $\exp[-it(E^{(0)} - E_{\rm out})]$. We write the general form in terms of an equivalent potential V as

$$\langle\alpha|U^{V,(1)}_{\rm cov}(t,-\infty)|\Psi^{(0)}\rangle = \langle\alpha|\frac{e^{-it(E^{(0)}-H_0)}}{E^{(0)}-H_0}V|\Psi^{(0)}\rangle = \frac{e^{-it(E^{(0)}-E^{(0)}_\alpha)}}{E^{(0)}-E^{(0)}_\alpha}\langle\alpha|V|\Psi^{(0)}\rangle. \tag{5.10}$$

Here the superscript $V,(1)$ denotes that we include the perturbation V to first order.

Ladder Expansion

The perturbation expansion of the covariant evolution-operator is very similar to that of the S-matrix due to their close connection according to Eqs. (5.1) and (5.4). This expansion contains all possible contractions of the field operators and is thus complete in the sense that all possible photon exchanges including self-energy and vacuum polarization effects (so-called *radiative corrections*) are generated.

We will in this work mainly be interested in that part of the perturbation expansion whose terms involve a series of equivalent potentials V_1, V_2, etc., appearing in a certain time-order. Such terms are *reducible* in the sense that they can be written as products of lower-order evolution operators, with the restriction that the intermediate states between the equivalent potentials are constructed from positive-energy solutions to the Dirac equation only (see Figure 5). We will refer to such an expansion, which is a part of the full expansion, as a *ladder expansion*.

It is shown in Ref. [16] that the n-th order term, containing a sequence of energy-dependent perturbations (equivalent potentials) $V_1(\mathcal{E})$, $V_2(\mathcal{E})$, ..., $V_n(\mathcal{E})$, in the lad-

der expansion of the covariant evolution-operator can be written as

$$U_{\rm cov}^{(n)}(t,-\infty)_{\rm ladder}P_{\mathcal{E}} = e^{-it(\mathcal{E}-H_0)}\left[\Gamma_+(\mathcal{E})V_n(\mathcal{E})\Gamma_+(\mathcal{E})V_{n-1}(\mathcal{E})\ldots\Gamma_+(\mathcal{E})V_1\right]P_{\mathcal{E}} \quad (5.11)$$

where $P_{\mathcal{E}}$ is the projection operator for the part of the model space with energy $\mathcal{E}$, and where $\Gamma_+(\mathcal{E})$ is the resolvent (Eq. 3.37) without negative-energy states. The resolvents appear after integration over the energy parameters of the intermediate electron propagators between the perturbations.

The total covariant evolution-operator can for a ladder expansion thus be written as

$$U_{\rm cov}(t,-\infty)_{\rm ladder}P_{\mathcal{E}} = e^{-it(\mathcal{E}-H_0)}\left[1+\sum_{n=1}^{\infty}\left\{\Gamma_+(\mathcal{E})V(\mathcal{E})\right\}^n\right]P_{\mathcal{E}} \quad (5.12)$$

where the various $V(\mathcal{E})$ are not neccesarily of the same kind.

Note that the resolvents appearing here are not restricted to the orthogonal Q space, and thus contain singular terms whenever an intermediate state is degenerate with the model state. These singularities will be removed in the Green's operator, which we will now introduce.

5.2 Definition of the Green's Operator

The perturbation expansion of the covariant evolution-operator contains singular terms due to the presence of intermediate model-space states and the resulting vanishing energy denominators from the propagators[2]. The original motivation for the introduction of the Green's operator was to remove these singularities in the covariant evolution-operator formalism.

In the single-electron case, the Green's operator $\mathcal{G}$ is defined as

$$U_{\rm cov}(t,t_0) = \mathcal{G}(t,t_0)\circ PU_{\rm cov}(0,t_0)P, \quad (5.13)$$

where P is the projection operator for the model space (Eq. 3.13), and where the significance of the multiplication symbol $\circ$ is that $\mathcal{G}$ should act on the *intermediate* model state (the P immediately to the right of $\circ$), whose energy might in general differ from that of the rightmost modelstate. In practice, this is thus only relevant when considering multidimensional model spaces. However, the definition is crucial in the derivation of the finite remainders after the model-space singularities are removed from the perturbation expansion, which will be discussed below.

The definition in the many-electron case is analogous, for example, in the two-electron case

$$U_{\rm cov}(t,t',t_0,t_0') = \mathcal{G}(t,t',t_0,t_0')\circ PU_{\rm cov}(0,0,t_0,t_0')P. \quad (5.14)$$

Before we consider the perturbation expansion of $\mathcal{G}$ we shall demonstrate that its definition implies that it acts as a wave operator for QED.

[2]These singularities appear also in the S-matrix formulation of bound-state QED, where they cancel among the terms in an expansion of the ratio in Sucher's level shift formula, Eq. (4.55).

Role as a Wave Operator

The starting point for this derivation is the conjecture that the time-evolution of the relativistic atomic state vector is given by the covariant evolution-operator in the equal-time approximation:

$$|\Psi(t)\rangle = NU_{\rm cov}(t,t_0)|\Psi(t_0)\rangle, \tag{5.15}$$

where N is a normalization constant. The plausiblity of this conjecture is supported in Refs. [16] and [13] by the fact that it leads to a time-dependence of the relativistic state vector which is of the form (in the interaction picture):

$$|\Psi(t)\rangle = e^{-it(E-H_0)}|\Psi(0)\rangle \tag{5.16}$$

where E is the *exact* energy, in accordance with the elementary quantum-mechanical result for an energy eigenstate.

Together with the definition of the Green's operator (Eqs. 5.13 and 5.14), the conjecture (5.15) can for $t_0 \to -\infty$ be written as

$$|\Psi(t)\rangle = N\mathcal{G}(t,-\infty)\circ PU_{\rm cov}(0,-\infty)P|\Phi\rangle \tag{5.17}$$

where

$$|\Phi\rangle = \lim_{t\to-\infty}|\Psi(t)\rangle \tag{5.18}$$

is the state to which the exact state tends as the perturbation is adiabatically switched off in the limit $t \to -\infty$ (see Eq. 4.54). For a one-dimensional model space, this state is equal to the model state,

$$|\Phi\rangle_{\text{1-dim.}} = |\Psi^{(0)}\rangle. \tag{5.19}$$

If we choose

$$N = \frac{1}{\langle\Psi^{(0)}|U_{\rm cov}(0,-\infty)|\Phi\rangle}, \tag{5.20}$$

the state $|\Psi(t)\rangle$ becomes intermediately normalized (see Eq. 3.10) at $t = 0$. Furthermore, with this choice for the normalization Eq. (5.17) reads

$$|\Psi(t)\rangle = \frac{\mathcal{G}(t,-\infty)\circ PU_{\rm cov}(0,-\infty)P|\Phi\rangle}{\langle\Psi^{(0)}|U_{\rm cov}(0,-\infty)|\Phi\rangle} = \mathcal{G}(t,-\infty)P\frac{U_{\rm cov}(0,-\infty)|\Psi^{(0)}\rangle}{\langle\Psi^{(0)}|U_{\rm cov}(0,-\infty)|\Psi^{(0)}\rangle}, \tag{5.21}$$

where the last step follows from the assumption of a one-dimensional model space (Eq. 5.19).

Gell-Mann and Low have shown [34] that if the state vector of a bound system evolves in time according to the (damped) evolution operator $U_\gamma(t,t_0)$, then the state vector defined by

$$|\Psi(t=0)\rangle = \lim_{\gamma\to0}\frac{U_\gamma(0,-\infty)|\Psi^{(0)}\rangle}{\langle\Psi^{(0)}|U_\gamma(0,-\infty)|\Psi^{(0)}\rangle} \equiv |\Psi\rangle, \tag{5.22}$$

is an exact solution to the full Hamiltonian $H = H_0 + H_{\rm int}$ of the bound system. Using this relation we can write Eq. (5.21) as

$$|\Psi(t)\rangle = \mathcal{G}(t,-\infty)P|\Psi\rangle. \tag{5.23}$$

But the definition of the P operator is $P|\Psi\rangle = |\Psi^{(0)}\rangle$, and we therefore have

$$|\Psi(t)\rangle = \mathcal{G}(t, -\infty)|\Psi^{(0)}\rangle, \tag{5.24}$$

and especially for $t = 0$

$$|\Psi(t=0)\rangle \equiv |\Psi\rangle = \mathcal{G}(0, -\infty)|\Psi^{(0)}\rangle. \tag{5.25}$$

The last equation says that the Green's operator evaluated at final time $t = 0$ acts as a wave operator, generating the exact state from its corresponding model state. This relation will be the starting point for our inclusion of QED effects into the atomic wavefunction.

The derivation given here is valid only for a one-dimensional model space, but can be generalized to case of an extended model space [13, 16].

5.3 Perturbation Expansion and Model-Space Contributions

We will now consider the perturbation expansion of $\mathcal{G}$ and see that the singularities in the covariant evolution-operator due to intermediate model states are removed by the definition (5.13). Based on the identification of $\mathcal{G}(0, -\infty)$ as a wave operator, we will only be interested in initial times $t_0 = -\infty$, and this time will not be explicitly stated below. Instead, we will explicitly indicate the energy-dependence of the operators, which follows from the definition of the multiplication operator $\circ$. We will in this section, for the sake of the derivation, assume that we are operating on an extended model space containing two energies $\mathcal{E}$ and $\mathcal{E}'$ with projection operators $P_\mathcal{E}$ and $P_{\mathcal{E}'}$. Furthermore, we assume that our expansion starts from the part $P_\mathcal{E}$ and that all intermediate model states are in $P_{\mathcal{E}'}$. For brevity, we will also drop the subscript "cov" from the covariant evolution-operator.

The zeroth-order covariant evolution operator is simply

$$U_\mathcal{E}^{(0)}(t) = e^{-it(\mathcal{E}-H_0)} \tag{5.26}$$

and thus fulfills $U_\mathcal{E}^{(0)}(0)P_\mathcal{E} = P_\mathcal{E}$. Using this fact we can expand the relation (5.13) as

$$\begin{aligned}
U_\mathcal{E}^{(0)}(t)P_\mathcal{E} =& \mathcal{G}_\mathcal{E}^{(0)}(t)P_\mathcal{E} \\
U_\mathcal{E}^{(1)}(t)P_\mathcal{E} =& \mathcal{G}_\mathcal{E}^{(1)}(t)P_\mathcal{E} + \mathcal{G}_{\mathcal{E}'}^{(0)}(t) \circ P_{\mathcal{E}'}U_\mathcal{E}^{(1)}(0)P_\mathcal{E} \\
U_\mathcal{E}^{(2)}(t)P_\mathcal{E} =& \mathcal{G}_\mathcal{E}^{(2)}(t)P_\mathcal{E} + \mathcal{G}_{\mathcal{E}'}^{(1)}(t) \circ P_{\mathcal{E}'}U_\mathcal{E}^{(1)}(0)P_\mathcal{E} + \mathcal{G}_{\mathcal{E}'}^{(0)}(t) \circ P_{\mathcal{E}'}U_\mathcal{E}^{(2)}(0)P_\mathcal{E} \\
U_\mathcal{E}^{(3)}(t)P_\mathcal{E} =& \mathcal{G}_\mathcal{E}^{(3)}(t)P_\mathcal{E} + \mathcal{G}_{\mathcal{E}'}^{(2)}(t) \circ P_{\mathcal{E}'}U_\mathcal{E}^{(1)}(0)P_\mathcal{E} + \mathcal{G}_{\mathcal{E}'}^{(1)}(t) \circ P_{\mathcal{E}'}U_\mathcal{E}^{(2)}(0)P_\mathcal{E} \\
&+ \mathcal{G}_{\mathcal{E}'}^{(0)}(t) \circ P_{\mathcal{E}'}U_\mathcal{E}^{(3)}(0)P_\mathcal{E}
\end{aligned} \tag{5.27}$$

etc, where $U^{(n)}$ and $\mathcal{G}^{(n)}$ contains n perturbations. Solving for $\mathcal{G}^{(n)}$ we find

$$\begin{aligned}
\mathcal{G}_\mathcal{E}^{(0)}(t)P_\mathcal{E} =& U_\mathcal{E}^{(0)}(t)P_\mathcal{E} \\
\mathcal{G}_\mathcal{E}^{(1)}(t)P_\mathcal{E} =& U_\mathcal{E}^{(1)}(t)P_\mathcal{E} - \mathcal{G}_{\mathcal{E}'}^{(0)}(t)P_{\mathcal{E}'}U_\mathcal{E}^{(1)}(0)P_\mathcal{E} \\
\mathcal{G}_\mathcal{E}^{(2)}(t)P_\mathcal{E} =& U_\mathcal{E}^{(2)}(t)P_\mathcal{E} - \mathcal{G}_{\mathcal{E}'}^{(0)}(t)P_{\mathcal{E}'}U_\mathcal{E}^{(2)}(0)P_\mathcal{E} - \mathcal{G}_{\mathcal{E}'}^{(1)}(t)P_{\mathcal{E}'}U_\mathcal{E}^{(1)}(0)P_\mathcal{E} \\
\mathcal{G}_\mathcal{E}^{(3)}(t)P_\mathcal{E} =& U_\mathcal{E}^{(3)}(t)P_\mathcal{E} - \mathcal{G}_{\mathcal{E}'}^{(0)}(t)P_{\mathcal{E}'}U_\mathcal{E}^{(3)}(0)P_\mathcal{E} - \mathcal{G}_{\mathcal{E}'}^{(1)}(t)P_{\mathcal{E}'}U_\mathcal{E}^{(2)}(0)P_\mathcal{E} \\
&- \mathcal{G}_{\mathcal{E}'}^{(2)}(t)P_{\mathcal{E}'}U_\mathcal{E}^{(1)}(0)P_\mathcal{E}
\end{aligned} \tag{5.28}$$

etc. The terms with negative sign in these expressions will remove the singularities due to intermediate model states, and furthermore leave a finite remainder known as a *model-space contribution* (MSC).

Based on the identification

$$U_{\mathcal{E}}^{(0)}(t) = \mathcal{G}_{\mathcal{E}}^{(0)}(t) = e^{-it(\mathcal{E}-H_0)} \tag{5.29}$$

and the resulting form of the ladder expansion (Eq. 5.11)

$$U_{\mathcal{E}}^{(n)}(t)_{\text{ladder}} P_{\mathcal{E}} = \mathcal{G}_{\mathcal{E}}^{(0)}(t) U_{\mathcal{E}}^{(n)}(0) P_{\mathcal{E}} = \mathcal{G}_{\mathcal{E}}^{(0)}(t) \left[\Gamma_+(\mathcal{E}) V(\mathcal{E})\right]^n P_{\mathcal{E}}, \tag{5.30}$$

the first-order MSC can be shown to be

$$\frac{\mathcal{G}_{\mathcal{E}'}^{(0)}(t) - \mathcal{G}_{\mathcal{E}}^{(0)}(t)}{\mathcal{E}' - \mathcal{E}} P_{\mathcal{E}'} V P_{\mathcal{E}} \equiv \frac{\delta \mathcal{G}_{\mathcal{E}}^{(0)}(t)}{\delta \mathcal{E}} P_{\mathcal{E}'} V P_{\mathcal{E}},$$

so that the first-order term $\mathcal{G}^{(1)}$ of the Green's operator becomes

$$\mathcal{G}_{\mathcal{E}}^{(1)}(t) P_{\mathcal{E}} = \mathcal{G}_{\mathcal{E}}^{(0)}(t) \Gamma_Q V P_{\mathcal{E}} + \frac{\delta \mathcal{G}_{\mathcal{E}}^{(0)}(t)}{\delta \mathcal{E}} P_{\mathcal{E}'} V P_{\mathcal{E}}. \tag{5.31}$$

Note that the intermediate model state is removed from the resolvent, $\Gamma \to \Gamma_Q$, and the MSC is the finite remainder after this removal. The difference ratio $\delta\mathcal{G}/\delta\mathcal{E}$ appearing here, discussed in detail in Appendix B of [14], turns into an ordinary energy-derivative when the intermediate state is completely degenerate with the model state. We we will assume this to be the case from now on.

The factor $P_{\mathcal{E}} V P_{\mathcal{E}}$ appearing in the MSC is the first-order term in the expansion of the effective interaction (to be discussed in the next section), and the first-order Green's operator can thus be written as

$$\begin{aligned} \mathcal{G}_{\mathcal{E}}^{(1)}(t) P_{\mathcal{E}} &= \mathcal{G}_{\mathcal{E}}^{(0)}(t) \Gamma_Q V P_{\mathcal{E}} + \frac{\partial \mathcal{G}_{\mathcal{E}}^{(0)}(t)}{\partial \mathcal{E}} P_{\mathcal{E}} W_{\text{eff}}^{(1)} P_{\mathcal{E}} \\ &= e^{-it(\mathcal{E}-H_0)} \Gamma_Q V P_{\mathcal{E}} - ite^{-it(\mathcal{E}-H_0)} P_{\mathcal{E}} W_{\text{eff}}^{(1)} P_{\mathcal{E}}. \end{aligned} \tag{5.32}$$

Evaluated at $t = 0$, this gives the first-order wave operator

$$\Omega_{\mathcal{E}}^{(1)} = \mathcal{G}_{\mathcal{E}}^{(1)}(0) P_{\mathcal{E}} = \Gamma_Q V P_{\mathcal{E}} \tag{5.33}$$

in complete agreement with the standard MBPT result (Eq. 3.39).

Similarly, the second-order term $\mathcal{G}_{\mathcal{E}}^{(2)}(t)$ evaluated at $t = 0$ gives, using that $\partial\Gamma_Q/\partial\mathcal{E} = -\Gamma_Q\Gamma_Q$, the second-order wave operator

$$\begin{aligned} \Omega_{\mathcal{E}}^{(2)} = \mathcal{G}_{\mathcal{E}}^{(2)}(0) P_{\mathcal{E}} &= \Gamma_Q V \Gamma_Q V P_{\mathcal{E}} + \left[\frac{\partial \mathcal{G}_{\mathcal{E}}^{(1)}(t)}{\partial \mathcal{E}}\right]_{t=0} P_{\mathcal{E}} W_{\text{eff}}^{(1)} P_{\mathcal{E}} \\ &= \Gamma_Q V \Gamma_Q V P_{\mathcal{E}} + \frac{\partial(\Gamma_Q V)}{\partial \mathcal{E}} P_{\mathcal{E}} W_{\text{eff}}^{(1)} P_{\mathcal{E}} \\ &= \Gamma_Q V \Gamma_Q V P_{\mathcal{E}} - \Gamma_Q \Omega_{\mathcal{E}}^{(1)} P_{\mathcal{E}} W_{\text{eff}}^{(1)} P_{\mathcal{E}} + \Gamma_Q \frac{\partial V}{\partial \mathcal{E}} P_{\mathcal{E}} W_{\text{eff}}^{(1)} P_{\mathcal{E}}. \end{aligned} \tag{5.34}$$

In the case that V is energy-independent, this expression reproduces the second-order wave operator from standard MBPT (Eq. 3.40). The expression given here is valid also inte the case that V is energy-dependent. Thus, the Green's operator method can be viewed as a generalization of MBPT to include energy-dependent perturbations. This is the crucial property which will allow us to construct a perturbation expansion of the wavefunction in which the equivalent energy-dependent potentials from QED can be included.

When applying the second-order expression (5.34) above, the two perturbations are generally not of the same kind. They may, for example, refer to a self-energy perturbation followed by a vacuum-polarization perturbation. A detailed derivation shows that the expression should be read in time-order, which means that $W_{\text{eff}}^{(1)}$ should only include the *first* perturbation, while $\Omega^{(1)}$ and the energy-derivative should refer only to the *last* perturbation.

In a similar fashion, the general expression for the n-th order term is [16]

$$\Omega^{(n)} = \Gamma_Q V_n \Omega^{(n-1)} + \sum_{m=1}^{n-1} \frac{\partial^* \Omega^{(m)}}{\partial \mathcal{E}} W_{\text{eff}}^{(n-m)} \tag{5.35}$$

where $\Omega^{(m)}$ is constructed from the m last perturbations in the sense of time order, while $W_{\text{eff}}^{(n-m)}$ is constructed by the $(n-m)$ first perturbations in the sequence. The asterisk denotes differentiation with respect to the very last perturbation (including the resolvent) $\Gamma_Q V_n$.

The model-space contributions can be shown to play a similar role for the Green's operator as do the folded terms for the wave operator in standard MBPT (see Eq. 3.46). That is, they are the terms in a Taylor expansion which corrects $\mathcal{G}$ for the shift in the energy of the model state due to the interaction.

5.4 The Effective Interaction

From the relation (5.16) we have, taking into account (5.24), that

$$\mathcal{G}(t, -\infty) = e^{-it(E-H_0)} \mathcal{G}(0, -\infty) \tag{5.36}$$

and the energy-shift induced by the interaction is thus given by

$$(E - E^{(0)})|\Psi^{(0)}\rangle = i \left[\frac{\partial}{\partial t} \mathcal{G}(t, -\infty) \right]_{t=0} |\Psi^{(0)}\rangle. \tag{5.37}$$

This means that we can define the effective interaction, operating in the model space, as

$$W_{\text{eff}} = P \left[i \frac{\partial}{\partial t} \mathcal{G}(t, -\infty) \right]_{t=0} P. \tag{5.38}$$

In each order n, the effective interaction (5.38) can be shown to be equal to

$$W_{\text{eff}}^{(n)} = P \tilde{\Omega}^{(n)} P \tag{5.39}$$

where $\tilde{\Omega}^{(n)}$ is the n-th order wave operator with its final resolvent removed:

$$\Omega^{(n)} = \Gamma_Q \tilde{\Omega}^{(n)}. \tag{5.40}$$

This is a form which is convenient for practical application. According to this relation, the first few orders become

$$\begin{aligned} W_{\text{eff}}^{(1)} &= PVP, \\ W_{\text{eff}}^{(2)} &= PV\Gamma_Q VP + \frac{\partial W_{\text{eff}}^{(1)}}{\partial \mathcal{E}} W_{\text{eff}}^{(1)}, \\ W_{\text{eff}}^{(3)} &= PV\Gamma_Q V\Gamma_Q VP + \frac{\partial W_{\text{eff}}^{(2)}}{\partial \mathcal{E}} W_{\text{eff}}^{(1)} + \frac{\partial W_{\text{eff}}^{(1)}}{\partial \mathcal{E}} PV\Gamma_Q VP. \end{aligned} \tag{5.41}$$

If the perturbations V contained in these terms are not of the same kind, the expressions should be read in time-order, with later times to the left. For example, in the second-order term the energy-derivative only affects the later of the perturbations. This result agrees with the S-matrix formalism and Sucher's level shift formula.

Connection to the Cross Section for Collision Processes

The topic of our published paper [37] is the application of the Green's operator formalism to compute cross sections for collision processes, in particular for the case of radiative recombination which will be one of the numerical applications considered in Chapter 7. The Green's operator is connected to the cross section via the well-known *optical theorem*, which we will first recall.

In terms of the S-matrix

$$S = 1 + iT \tag{5.42}$$

and the corresponding scattering amplitude τ

$$\langle q|T|p\rangle = 2\pi\delta(E_p - E_q)\tau(p \to q), \tag{5.43}$$

the optical theorem is [28]

$$2\text{Im}\langle p|T|p\rangle = \sum_q |2\pi\delta(E_p - E_q)\tau(p \to q)|^2. \tag{5.44}$$

Since the cross section for a particular process $p \to q$ is proportional to $|\tau(p \to q)|^2$, this theorem states that the imaginary part of the *forward scattering amplitude* $\langle p|T|p\rangle$ is directly related to the total cross section.

As mentioned above, the perturbation expansion of the S-matrix in the bound-state case contains singular terms due to intermediate states which are degenerate in energy with the initial state. Thus, the S-matrix cannot be used directly in the optical theorem if bound states are present.

In Appendix A we derive a relation between the forward scattering amplitude and the effective interaction (considering the state $|p\rangle$ as the model state):

$$PTP = -2\pi\delta(E_{\text{in}} - E_{\text{out}})W_{\text{eff}}. \tag{5.45}$$

This relation can be used to construct the forward scattering amplitude from the Green's operator, and this is then valid also in the bound-state case. The effective interaction, and thus also the forward scattering amplitude, will aquire an imaginary part whenever an intermediate many-particle state is degenerate with the initial state, which is familiar from elementary scattering theory in quantum mechanics.

The relation (5.45) is the main result of our paper, Ref. [37].

5.5 Theory of QED-effects in Wavefunctions: Summary

We will end this chapter and Part I of the thesis with a brief summary of the theory discussed so far and how it can be used to construct QED corrections to atomic wavefunctions and energies.

- In Chapter 2 we reviewed how the Dirac equation can be used to describe a single relativistic electron influenced only by the potential from an atomic nucleus. The solutions to this equation are used to construct model states which are the zeroth-order approximations to the exact states.

- In Chapter 3 we saw how standard many-body perturbation theory (MBPT) can be used to construct a wave operator Ω which generates the exact wavefunction and energy of a many-electron system, in the approximation that the interaction between the electrons is instantaneous (energy-independent).

- In Chapter 4 we saw that, based on QED, the photon-mediated interactions among the atomic electrons can be described by energy-dependent equivalent potentials. These potentials describe both the interelectronic interaction as well as the self-interaction of each electron.

- In this chapter we have learned that the energy-dependent potentials from QED can be included in an expansion of the Green's operator $\mathcal{G}$, which acts as an energy-dependent wave operator $\Omega_{\mathcal{E}}$. The formalism developed in this chapter allows us to construct this operator perturbatively, and from it obtain QED corrections to the atomic wavefunction and energy.

In practice, one needs a particular representation of the wave operator, and its construction typically proceeds by directly computing the corrections to the wavefunction in a suitable representation. We then also gain access to the corresponding energy shift by using the expression for the effective interaction in Eq. (5.39).

Part II
Applications

The second part of the thesis concerns applications of the formalism discussed in Part I. First we will construct a perturbation expansion of the Green's operator for heliumlike systems, in which we include arbitrarily many interelectronic Coulomb interactions in combination with a single retarded photon (self-energy, vacuum-polarization and single-photon exchange). This allows us to compute the lowest-order combined effect of electron correlation and QED. This work is described in our recent publication, Ref. [38].

We will then use the numerical method for the inclusion of self-energy and vacuum-polarization into a single-electron wavefunction to compute QED corrections to transition amplitudes for two atomic processes in hydrogenlike uranium. The two processes are radiative recombination, in which we compute corrections to the differential cross section and polarization of the emitted radiation, and radiative decay where we compute corrections to the ratio $\tau_{\mathrm{M2}}/\tau_{\mathrm{E1}}$ of the magnetic quadrupole and electric dipole amplitudes. This work is described in a manuscript which has recently been submitted to Phys. Rev. A [39].

Finally, we will present our results and give a summary of the thesis as well as provide an outlook for further research.

6 Combined QED and Correlation in Heliumlike Ions

Heliumlike ions are interesting since they are the simplest many-electron atomic systems, and thus serve as an ideal testing ground for the study of many-body effects such as electron correlation[3]. Furthermore, as the nuclear charge number Z increases the effects of relativity and QED become increasingly important. For low Z, it is of vital importance to treat electron correlation accurately, either by the use of variational methods of by some variant of many-body perturbation theory. It is typically sufficient to include the effects of QED only approximately, for example using hydrogenic results modified by a screening potential [40–42].

For large Z, on the other hand, the QED effects are more important than correlation, and methods based on bound-state QED are needed. To date, the most comprehensive bound-state QED study of heliumlike ions is that of Artemyev *et al.* [43] which rigorously includes all effects up to and including the two-photon level in a numerical calculation based on the two-time Green's function technique of Shabaev [32].

In the intermediate Z range ($Z \approx 10$ to $Z \approx 30$) it has been argued [44,45] that it might be neccesary to treat correlation and the QED effects in a unified manner. In this chapter we will apply the Green's operator from the covariant evolution-operator formalism to compute the energy shift in the ground state of heliumlike ions due to the combined effect of correlation and QED. We accomplish this by constructing a perturbation expansion which includes arbitrarily many Coulomb interactions together with a single "QED-photon" (self-energy, vacuum-polarization, or single photon exchange). The part due to single photon exchange was treated in the PhD thesis of Daniel Hedendahl [46], and in this work we compute the contribution due to self-energy and vacuum polarization.

We note that much of the material in this chapter will be presented in a way which closely resembles that of our recent publication [38], sometimes quoting entire paragraphs.

6.1 Preliminaries

The model Hamiltonian we will choose for our heliumlike system is a sum of two Dirac Hamiltonians including the nuclear potential:

$$H_0 = \sum_{j=1}^{2} \left[-i\boldsymbol{\alpha} \cdot \nabla_j - eV_{\text{nuc.}}(r_j) + \beta m \right]. \tag{6.1}$$

We will here only consider corrections to the ground state, which is described by the antisymmetric model state

$$|\Psi^{(0)}\rangle = \frac{1}{\sqrt{2}}\Big(|\psi_{1s\uparrow}\psi_{1s\downarrow}\rangle - |\psi_{1s\downarrow}\psi_{1s\uparrow}\rangle \Big) = |\tilde{\psi}_{1s}\tilde{\psi}_{1s}\rangle \left[\frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \Big) \right], \tag{6.2}$$

[3]We will in this work consider as correlation all terms in the perturbation expansion which contain at least two interelectron-interactions.

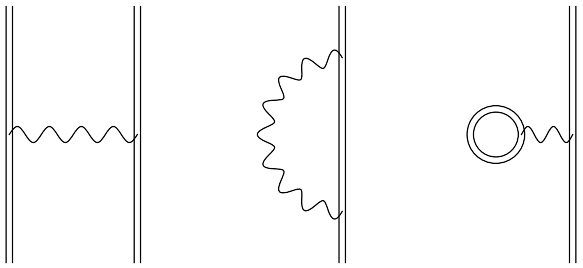


Figure 6: The single-photon perturbations included in $V(\mathcal{E})$, from left to right: single-photon exchange, self-energy, and vacuum-polarization.

where the arrows denote spin projection and where $\tilde{\psi}$ are the spin-independent parts of the single-electron states. In our computational scheme, we will consider a perturbation expansion starting from the state $|\tilde{\psi}_{1s}\tilde{\psi}_{1s}\rangle$ where the angular momenta of the individual electrons are uncoupled. Only after having constructed the perturbation expansion to desired order will we couple the initial state (and the final state, if we are computing an energy correction) to the correct total angular momentum J with projection M, which are both equal to 0 for the ground state. In the expressions that follow, we will let $|ab\rangle$ denote the uncoupled model state.

The (energy-dependent) perturbation will be taken to consist of three terms

$$V(\mathcal{E}) = V_{\mathrm{SPE}}(\mathcal{E}) + \Sigma_{\mathrm{ren}}(\mathcal{E}) + U_{\mathrm{VP}}^{\mathrm{ren}} \tag{6.3}$$

which are, respectively, the equivalent potential for single photon exchange, the renormalized self-energy operator, and renormalized vacuum-polarization potential. This approximation of $V(\mathcal{E})$ corresponds to considering only single-photon perturbations (see Figure 6).

Both the potential for single photon exchange and the self-energy operator, apart from being energy-dependent, are also gauge-dependent. In the Coulomb gauge, the single photon exchange potential has the form

$$V_{\mathrm{SPE}}^{\mathrm{Cou}}(\mathcal{E}) = V_{\mathrm{C}} + V_{\mathrm{T}}(\mathcal{E}) \tag{6.4}$$

where the scalar part V_{C} is the energy-independent, instantaneous Coulomb interaction

$$V_{\mathrm{C}} = \frac{e^2}{4\pi r_{12}} \tag{6.5}$$

and $V_{\mathrm{T}}(\mathcal{E})$ is the energy-dependent transverse part given by Eq. (4.73) with the appropriate Coulomb-gauge function $f(|\mathbf{k}|)$.

The instantaneous Coulomb interaction can be treated numerically to arbitrary order using the techniques of standard many-body perturbation theory (Chapter 3), and represents most of the interelectronic interaction, especially for the lighter nuclei (see Figure 7). The transverse part is much more demanding to evaluate numerically, and we will therefore separate out the part representing the Coulomb interaction and write the entire perturbation (6.3) in Coulomb gauge as

$$V(\mathcal{E}) = V_{\mathrm{C}} + V_{\mathrm{QED}}(\mathcal{E}) \tag{6.6}$$

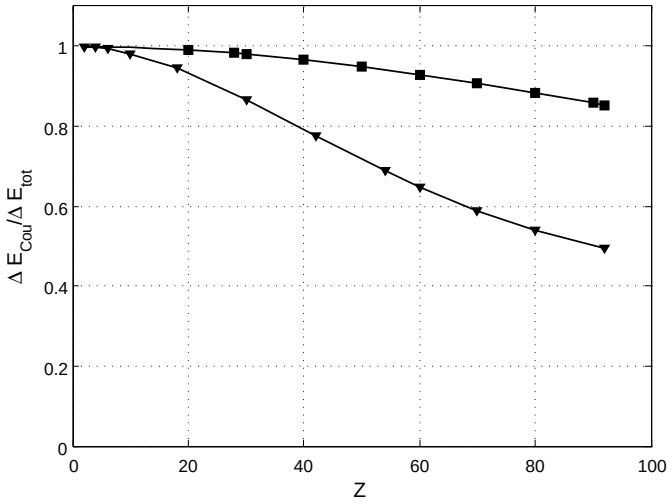


Figure 7: The relative contribution to the energy shift of the ground state of heliumlike ions from the Coulomb interaction only, for the case of single photon exchange (squares) and two-photon exchange (triangles). 1-photon: Artemyev *et al.* [47]; 2-photon: Lindgren *et al.* [48]

where

$$V_{\mathrm{QED}}(\mathcal{E}) = V_{\mathrm{T}}(\mathcal{E}) + \Sigma_{\mathrm{ren}}(\mathcal{E}) + U_{\mathrm{VP}}^{\mathrm{ren}} \tag{6.7}$$

contains the energy-dependent QED effects which lie beyond standard MBPT. Our approach to computing the combined effect of correlation and QED will be to approximate the correlation by a series of Coulomb interactions V_{C}.

6.2 The Pair Function with QED Corrections

In order to compute the energy shift due to the combination of correlation and QED we wish to treat the Coulomb interaction to high order while retaining the QED effects only to first order. To this end, we consider an expansion of the wave operator $\Omega = \mathcal{G}(0, -\infty)$ in terms of the number of retarded photons together with arbitrarily many Coulomb interactions:

$$\Omega = 1 + \Omega_{\mathrm{C}} + \Omega_{\mathrm{C}}^{1\mathrm{ph}} + \Omega_{\mathrm{C}}^{2\mathrm{ph}} + \ldots \tag{6.8}$$

Here, Ω_{C} contains only Coulomb interactions while $\Omega_{\mathrm{C}}^{1\mathrm{ph}}$ contains a single retarded photon (given by V_{QED}) together with arbitrarily many Coulomb interactions, $\Omega_{\mathrm{C}}^{2\mathrm{ph}}$ contains a two retarded photons together with arbitrarily many Coulomb interactions, and so on.

The part we are interested in is $\Omega_{\mathrm{C}}^{1\mathrm{ph}}$. The perturbation expansion for this part can be formulated from the definitions given in Chapter 5. However, computing each term in the perturbation expansion explicitly would require the evaluation of expressions involving an ever-increasing number of Coulomb interactions together with the retarded photon, including model-space contributions. In order to avoid this, a recursive equation for the wave (Green's) operator can be formulated which

includes $V_{\rm C}$ recursively but where $V_{\rm QED}$ appears non-recursively. By iteratively solving such an equation, an infinite sequence of Coulomb interactions will be generated while the QED effects are treated to first order only.

The equation we are looking for was derived in Refs. [14] and [16]. Assuming that we have already generated Ω_C (the wave operator corresponding to arbitrarily many Coulomb interactions) and the corresponding effective interaction $W_{\rm C} = PV_{\rm C}\Omega_{\rm C}P$ using the methods in Chapter 3, we can write the equation as

$$\begin{aligned}\Omega_{\rm C}^{\rm 1ph} = \Gamma_Q V_{\rm QED}\Omega_{\rm C} + \Gamma_Q \sum_{n=1}^{\infty} \frac{\delta^n V_{\rm QED}}{\delta \mathcal{E}^n}\Omega_{\rm C}(W_{\rm C})^n \\ + \Gamma_Q V_{\rm C}\Omega_{\rm C}^{\rm 1ph} - \Gamma_Q \Omega_{\rm C}^{\rm 1ph} W_{\rm C} - \Gamma_Q \Omega_{\rm C} W_{\rm C}^{\rm 1ph}. \end{aligned} \tag{6.9}$$

The first two terms of this equation account for the inclusion of a single retarded photon (described by $V_{\rm QED}$) to the Coulomb ladder contained in $\Omega_{\rm C}$. The sum in the second term generates all the model-space contributions (MSC) due to model states present in $\Omega_{\rm C}$ (see Ref. [14]). Once these two terms are computed, the retarded photon has been included into $\Omega_{\rm C}^{\rm 1ph}$, and they need not be considered further.

On the other hand, the last three terms on the right-hand side of (6.9) contain $\Omega_{\rm C}^{\rm 1ph}$, which is the operator we are looking to construct, and can thus be computed iteratively. These terms describe the inclusion of an additional Coulomb interaction to the wave operator $\Omega_{\rm C}^{\rm 1ph}$, and by iteratively updating them we will generate a sequence of Coulomb interactions *after* the retarded photon (see Figure 10).

In order to implement Eq. (6.9) numerically, we represent it as a correction to the model-state $|ab\rangle$. The first step is to generate a representation of $\Omega_{\rm C}$. By acting on the model state with the iterative form of the wave operator for energy-independent perturbations (Eq. 3.50) we obtain the so-called *pair equation* [49–51]

$$|\rho_{\rm ab,C}\rangle = \Gamma_Q V_C|ab\rangle + \Gamma_Q V_C|\rho_{\rm ab,C}\rangle - \Gamma_Q|\rho_{\rm ab,C}\rangle W_{\rm C}. \tag{6.10}$$

By iteratively solving this equation we obtain the *pair function*

$$|\rho_{\rm ab,C}\rangle = (\Omega_{\rm C} - 1)|ab\rangle \tag{6.11}$$

which contains a ladder expansion of Coulomb interactions (see Figure 8).

We also define the *extended* pair function (see Figure 9)

$$|\Psi_{\rm ab,C}\rangle = \Omega_{\rm C}|ab\rangle = |ab\rangle + |\rho_{\rm ab,C}\rangle \tag{6.12}$$

which is the exact state in the (no-virtual-pair) Coulomb approximation, and serves as our representation of $\Omega_{\rm C}$. The corresponding effective interaction $W_{\rm C}$ can be obtained from the relation (5.39).

Having obtained $|\Psi_{\rm ab,C}\rangle$ we can proceed to generate the full wave operator $\Omega_{\rm C}^{\rm 1ph}$. Using the explicit form of the reduced resolvent for the model Hamiltonian (6.1)

$$\Gamma_Q = \sum_{rs\neq ab} \frac{|rs\rangle\langle rs|}{E_a + E_b - E_r - E_s}, \tag{6.13}$$

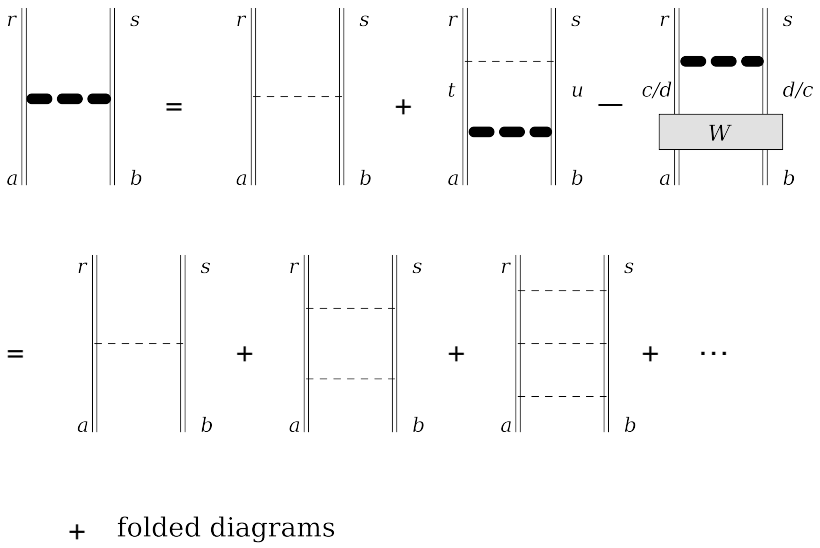


Figure 8: The pair equation in diagrammatic form. The thin dashed lines represent the Coulomb interaction and the heavy dashed lines represent the accumulated effect of correlation. The last term of the top row (the "folded" term) is given in the general form which allows for intermediate model-states $|cd\rangle$ which may be different from $|ab\rangle$ (an extended model-space). Iterating this equation until convergence gives the ordinary pair function $|\rho_{ab,\mathrm{C}}\rangle$ which contains an infinite ladder of Coulomb interactions including folded terms (taken from Ref. [38]).

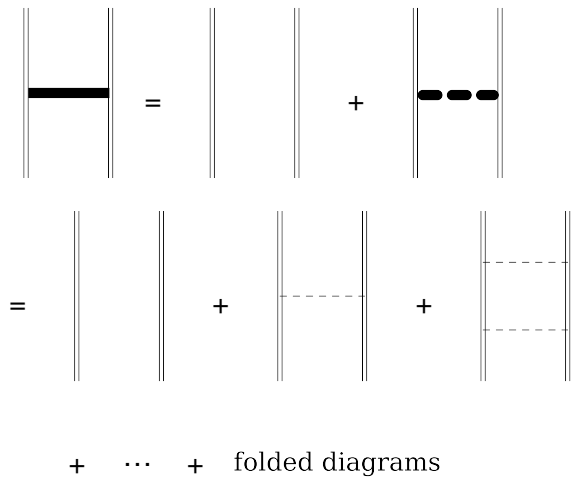


Figure 9: The extended pairfunction $|\Psi_{ab,\mathrm{C}}\rangle = |ab\rangle + |\rho_{ab,\mathrm{C}}\rangle$ is equal to the exact two-electron state in the (no-virtual-pair) Coulomb-approximation. (Taken from Ref. [38])

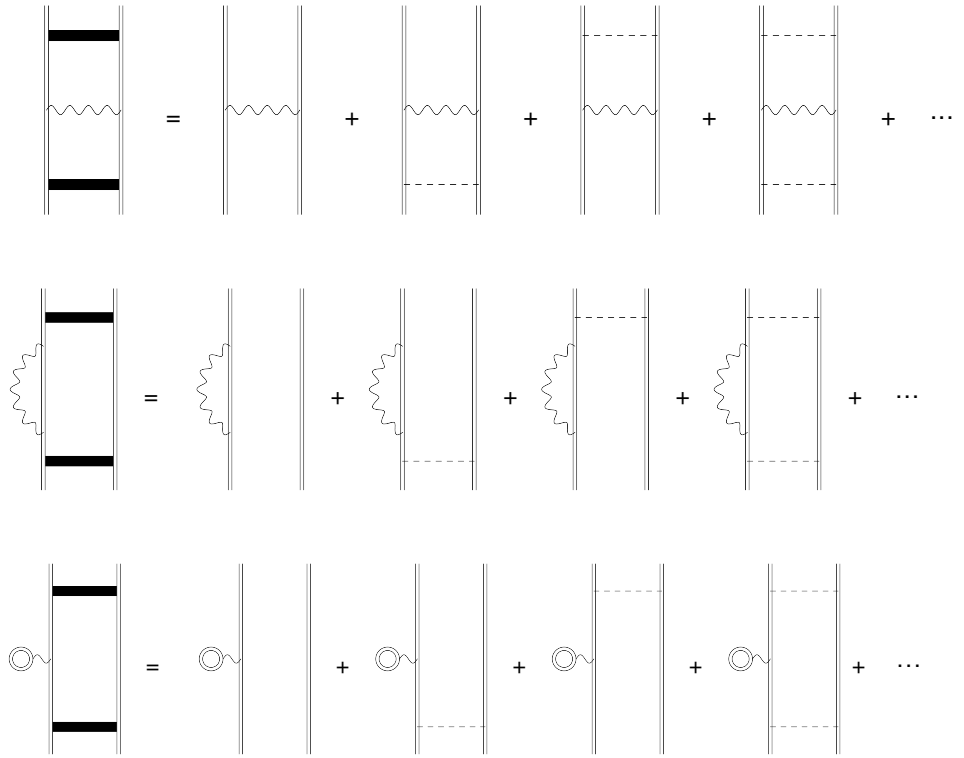


Figure 10: Three different pair functions containing a single retarded photon (photon-exchange, self-energy, or vacuum-polarization) together with arbitrarily many Coulomb-interactions including model-space contributions (taken from Ref. [38]).

we find that a representation of (6.9) is given by

$$(E_a + E_b - E_r - E_s)\langle rs|\rho^{\rm 1ph}_{\rm ab,C}\rangle = \langle rs|V_{\rm QED}|\Psi_{\rm ab,C}\rangle + \sum_{n=1}^{\infty}\langle rs|\frac{\partial^n V_{\rm QED}}{\partial\mathcal{E}^n}|\Psi_{\rm ab,C}\rangle (W_{\rm C})^n + \langle rs|V_{\rm C}|\rho^{\rm 1ph}_{\rm ab,C}\rangle - \langle rs|\rho^{\rm 1ph}_{\rm ab,C}\rangle W_{\rm C} - \langle rs|\rho_{\rm ab,C}\rangle W^{\rm 1ph}_{\rm C}. \quad (6.14)$$

Here, the function

$$|\rho^{\rm 1ph}_{\rm ab,C}\rangle = \Omega^{\rm 1ph}_{\rm C}|ab\rangle \quad (6.15)$$

is a pair function which is corrected by precisely one retarded photon (see Figure 10).

6.3 The Energy Shift

The energy-shift induced in the state $|ab\rangle$ due to the effects included in $\Omega^{\rm 1ph}_{\rm C}$ can be computed using the relation (5.39) for the effective interaction by evaluating the right-hand side of (6.14) with $\langle rs|$ replaced by $\langle ab|$. We are interested in isolating that part of the energy shift which contains at least two Coulomb-interactions (correlational effects). In order to do this we compute the difference

$$\Delta E_{\rm QED\ corr.} = \Delta E^{\rm 1ph}_{\rm C} - \Delta E^{\rm 1ph} - \Delta E^{\rm 1ph}_{\rm 1C\ after} - \Delta E^{\rm 1ph}_{\rm 1C\ before} \quad (6.16)$$

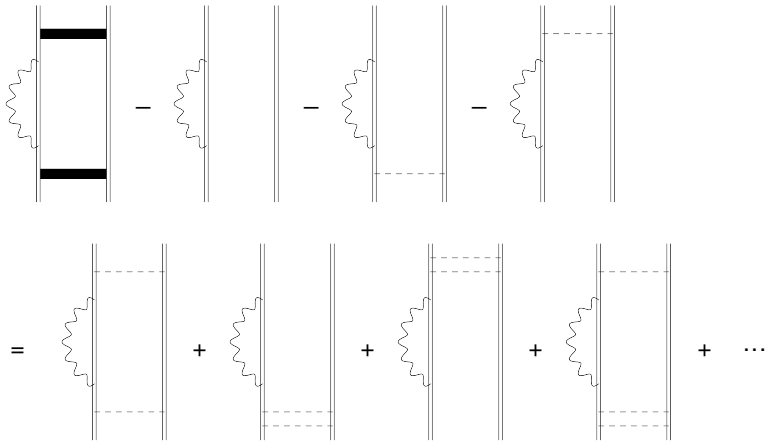


Figure 11: Effects containing at least two Coulomb interactions (correlational effects) are calculated as the difference between the energy-shift due to the fully correlated one-photon wave operator and the three lowest-order approximations. (Taken from Ref. [38])

where $\Delta E_{\mathrm{C}}^{1\mathrm{ph}}$ is the energy shift due to the fully correlated, single-retarded-photon wave operator $\Omega_{\mathrm{C}}^{1\mathrm{ph}}$, $\Delta E^{1\mathrm{ph}}$ is the energy shift due only to the retarded photon, and $\Delta E_{1\mathrm{C\ after}}^{1\mathrm{ph}}$ and $\Delta E_{1\mathrm{C\ before}}^{1\mathrm{ph}}$ are the energy shifts for the retarded photon together with a single Coulomb interaction (after and before, respectively). This difference is illustrated in Figure 11 for the case of a self-energy photon.

The second-order energy shifts $\Delta E_{1\mathrm{C\ after}}^{1\mathrm{ph}}$ and $\Delta E_{1\mathrm{C\ before}}^{1\mathrm{ph}}$ which appear in the difference (6.16) can be compared with two-photon results in the literature and thereby function as a test of our numerical method. Of particular interest are our results for the screened self-energy at the two-photon level, which we compute in both the Feynman and Coulomb gauges. A detailed comparison of these two calculations will be presented in Section 8.1.

6.4 Method

We will now describe our computation of the QED-corrected pair function and the corresponding energy shift discussed above. Our numerical method is based on a finite basis set of solutions to the discretized Dirac equation. The numerical implementation of Eq. (6.14) involves evaluation of matrix elements of the various interactions and their energy-derivatives with respect to the basis functions. The radial parts of these integrals are computed numerically while the spin-angular parts are treated analytically using angular-momentum graphs (unfortunately, a description of the graphical angular-momentum technique would be much too lengthy to include here, instead we refer to Ref. [24] for details).

6.4.1 Solving the Radial Dirac Equation

We solve the radial part of the Dirac equation (see, e.g., Ref. [22]) using the numerical method described in Ref. [51]. A complete numerical spectrum of states is obtained

Table 1: Values of the nuclear radii used in this work.

Z	R_{nuc} [fm]
14	3.123
18	3.423
24	3.643
30	3.928
50	4.654

by solving the radial equation for each κ,

$$\begin{pmatrix} -eV_{\text{nuc}}(r) + m & -\frac{d}{dr} + \frac{\kappa}{r} \\ \frac{d}{dr} + \frac{\kappa}{r} & -eV_{\text{nuc}}(r) - m \end{pmatrix} \begin{pmatrix} F_{n,\kappa}(r) \\ G_{n,\kappa}(r) \end{pmatrix} = E_{n,\kappa} \begin{pmatrix} F_{n,\kappa}(r) \\ G_{n,\kappa}(r) \end{pmatrix}, \tag{6.17}$$

on a discretized radial grid with $r_0 < r < R$. The parameters r_0 and R are chosen small/large enough that their particular values do not influence the final results. Solving this equation on a grid of N grid points gives a set of $2N$ orthogonal radial eigenfunctions and their eigenvalues. The first few positive-energy solutions accurately represent the lowest bound states in a hydrogenlike ion. However, due to the artificial confinement of the problem into a spherical cavity, the highly excited solutions do not correspond to any physical state but serve only to provide a complete solution-set in the discretized space.

The effect from the finite nuclear radius is incorporated directly into our wavefunctions by modifying the $1/r$ dependence of the nuclear potential inside some radius R_{nuc}. We model the nucleus as a homogeneous ball of charge; the radii for the nuclei considered in this work are given in Table 1.

By extrapolating the final results obtained from radial basis functions on increasingly fine radial grids, the continuum limit can be found. For further details on the space-discretization method for the Dirac equation, see Ref. [51].

6.4.2 The Coulomb Interaction

It is well-known that the matrix element of the Coulomb interaction can, using the Wigner-Eckart theorem, be written in terms of reduced single-electron matrix elements as

$$\langle rs|V_{\text{C}}|tu\rangle = \sum_{k=0}^{\infty} (-1)^k \langle j_r||\boldsymbol{C}^k||j_t\rangle \langle j_s||\boldsymbol{C}^k||j_u\rangle R_k A_1 \tag{6.18}$$

where j_i is the total angular-momentum of each respective state.

Here $\boldsymbol{C}^k$ is a spherical tensor of rank k whose elements are defined in terms of the ordinary spherical harmonics Y_m^l as

$$C_q^k = \sqrt{\frac{4\pi}{2k+1}} Y_q^k. \tag{6.19}$$

The reduced matrix element of this tensor is given in terms of a 3-j symbol (see e.g. Ref. [52]; note however that the sl-coupling scheme is employed in that reference):

$$\langle j_r||\boldsymbol{C}^k||j_t\rangle = (-1)^{j_r - \frac{1}{2}} \sqrt{(2j_r+1)(2j_t+1)} \begin{pmatrix} j_r & k & j_t \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \tag{6.20}$$

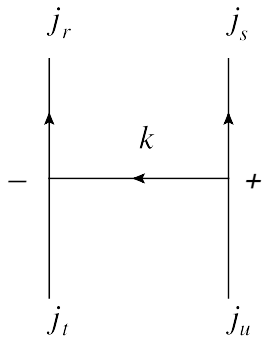


Figure 12: Angular-momentum graph corresponding to the factor A_1 in Eq. (6.18).

This expression vanishes unless the triangular condition $|j_r - j_t| \leq k \leq j_r + j_t$ is fulfilled, and an implicit parity constraint requires that the sum $l_r + l_t + k$ is even.

R_k is the radial integral

$$\begin{aligned} R_k &= \frac{e^2}{4\pi} \int dr_1 \int dr_2 \; \phi_r^\dagger(r_1)\phi_s^\dagger(r_2)\frac{r_<^k}{r_>^{k+1}}\phi_t(r_1)\phi_u(r_2) \\ &= \frac{e^2}{4\pi} \int dr_1 \int dr_2 \; \frac{r_<^k}{r_>^{k+1}} \\ &\quad \times \left[F_r(r_1)F_t(r_1) + G_r(r_1)G_t(r_1)\right]\left[F_s(r_2)F_u(r_2) + G_s(r_2)G_u(r_2)\right] \end{aligned} \tag{6.21}$$

in which $r_<$ ($r_>$) is the lesser (greater) of the two radial coordinates. This integral is computed by interpolating the discretized radial basis functions to continous space using Lagrange polynomials.

A_1 is an angular factor which can be represented by the angular-momentum graph in Figure 12. The graphs from successive Coulomb interactions in the perturbation expansion are coupled and can be reduced to the form A_1 according to the rules given in [24]. In this way, the pair function at a certain stage in the expansion can always be associated with an angular-momentum graph such as that in Figure 12, and this simplifies the final coupling of the individual electrons to the desired JM-state.

6.4.3 The Transverse Photon Potential

The matrix element of the transverse photon potential $V_{\rm T}(\mathcal{E})$ is given in Eq. (4.73), where in Coulomb gauge the function $f(k)$ is given by

$$f(\mathbf{x}_1, \mathbf{x}_2, k) = \frac{e^2}{4\pi^2}\left[\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 \frac{\sin(kr_{12})}{r_{12}} - (\boldsymbol{\alpha}_1 \cdot \boldsymbol{\nabla}_1)(\boldsymbol{\alpha}_2 \cdot \boldsymbol{\nabla}_2)\frac{\sin(kr_{12})}{k^2 r_{12}}\right]. \tag{6.22}$$

Here, $k = |\mathbf{k}|$ is the linear momentum of the photon.

In analogy with the Coulomb interaction, the matrix elements of $V_{\rm T}(\mathcal{E})$ can be expanded into a sum of partial waves using the identity

$$\frac{\sin(kr_{12})}{kr_{12}} = \sum_{l=0}^{\infty}(2l+1)j_l(kr_1)j_l(kr_2)\mathbf{C}^l(\theta_1,\varphi_1)\cdot\mathbf{C}^l(\theta_2,\varphi_2) \tag{6.23}$$

where l is the orbital angular momentum of the photon and j_l are the spherical Bessel functions. The contribution from the first term of (6.22) is known as the *Gaunt term* and that from the second term is known as the *scalar retardation term*. Together, these two terms are known as the *Breit interaction*. The expressions $(\boldsymbol{\alpha}\cdot\boldsymbol{\nabla})j_l(kr)\boldsymbol{C}^l$ appearing in the scalar retardation term can be transformed into a form involving products of $j_{l\pm1}(kr)$, $\boldsymbol{\alpha}$, and $\boldsymbol{C}^{l\pm1}$ (see Ref. [14]), where $\boldsymbol{\alpha}$ and $\boldsymbol{C}^{l\pm1}$ are coupled into a tensor of rank l. The evaluation of the spin-angular part of the matrix-element $\langle rs|V_{\rm T}(\mathcal{E})|tu\rangle$ in terms of angular-momentum graphs is considered in Ref. [48].

For each k, the radial integrals over r_1 and r_2 are performed by interpolating the basis functions using Lagrange polynomials. In each radial subinterval $[r_i, r_{i+1}]$, integrals of the form

$$\int_{r_i}^{r_{i+1}} dr\; r^m j_l(kr) \tag{6.24}$$

must then be performed. This is accomplished by treating the $l = m = 0$ case numerically, then using the recursion relations

$$\begin{aligned} j_l(x) &= \left(\frac{l-1}{l}\right) j_{l-2}(x) - \left(\frac{2l-1}{l}\right)\frac{d}{dx}\left[j_{l-1}(x)\right] \\ x^{m+1}j_l(x) &= (l-m+1)x^m j_{l+1}(x) + \frac{d}{dx}\left[x^{m+1}j_{l+1}(x)\right] \\ j_l(x) &= \left(\frac{2l+3}{x}\right) j_{l+1}(x) - j_{l+2}(x) \end{aligned} \tag{6.25}$$

for the other cases [25]. The final integral over k is performed using Gauss-Legendre quadrature with a cutoff taken large enough that its particular value does not influence the results.

6.4.4 The Electron Self-Energy

The two-electron matrix elements of the renormalized self-energy operator are

$$\langle rs|\Sigma_{\rm ren}(\mathcal{E})|tu\rangle = \delta_{u,s}\langle r|\Sigma_{\rm ren}(\mathcal{E}-E_u)|t\rangle + \delta_{t,r}\langle s|\Sigma_{\rm ren}(\mathcal{E}-E_t)|u\rangle. \tag{6.26}$$

As described in Appendix B, the single-electron matrix elements appearing here can be computed using an expansion in terms of the scattering-order with the nuclear potential [53, 54]. They are then written as the sum of a zero-, one-, and many-potential term:

$$\langle r|\Sigma_{\rm ren}|t\rangle = \Sigma^{\rm ZP}_{rt} + \Sigma^{\rm OP}_{rt} + \Sigma^{\rm MP}_{rt}. \tag{6.27}$$

The zero- and one-potential terms are in this scheme defined in momentum space, while the remaining many-potential term can be calculated in coordinate space using the rules of bound-state QED. Explicit expressions for these terms are given in Feynman gauge in Ref. [55], and in Coulomb gauge in Refs. [56] and [30]. These expressions are rather lengthy and we will not repeat them here. The general form of the zero- and one-potential terms in Coulomb gauge are given in Appendix C.

The zero- and one-potential terms can in principle be obtained by Fourier-transforming the states $|t\rangle$ and $|r\rangle$ to momentum space. This works well for the

lowest bound states, but the highly excited states obtained with the space discretization method acquire large contributions from a wide range of momenta. Together with the oscillatory behaviour and slow decay of the integrands, this means that the numerical evaluation of the zero- and one-potential terms is difficult to perform without introducing large numerical errors.

Instead, we find it convenient to work directly with the single-coordinate representations of the incoming extended pair function $\langle r_1|\Psi_{ab,\mathrm{C}}\rangle$ and the outgoing reduced resolvent (where the state $|u\rangle$ of the "spectator" electron is kept fixed)

$$\langle r_1'|\Gamma_Q(\mathcal{E}-E_u)|r_1\rangle = \Gamma_Q(\mathcal{E}-E_u,r_1',r_1) = \sum_n \frac{\langle r_1'|n\rangle\langle n|r_1\rangle}{\mathcal{E}-E_u-E_n}. \tag{6.28}$$

Both these functions are relatively smooth and localized and their numerical Fourier transforms can be constructed without too much difficulty. For example, the Fourier transform with respect to r_1 of the outgoing resolvent is

$$\Gamma_Q(\mathcal{E}-E_u,r_1',p) = \sqrt{\frac{2}{\pi}}\int dr_1\ (r_1)^2(-i)^l j_l(pr_1)\sum_n \frac{\Phi_n(r_1')\Phi_n^\dagger(r_1)}{\mathcal{E}-E_u-E_n}\,, \tag{6.29}$$

where l is given by the orbital angular-momentum of the particular component (large or small) of the state Φ_n that is considered. The integral over the spherical Bessel function can be computed using the same method as in the transverse-photon case above. Having obtained the Fourier transformations, the zero- and one-potential terms for the incoming pair function and outgoing resolvent can be calculated in terms of momentum-integrals for each outgoing r_1', which we perform numerically using Gauss-Legendre quadrature. The contributions from these terms are thus functions of the outgoing radial coordinate r_1', and their evaluation is discussed in more detail in Appendix C.

The many-potential term can be formulated directly from the definition of the self-energy operator (Eq. 4.77) and the expansion of the electron propagator in Eq. (B.1). It is however most conveniently expressed, not directly in terms of the many-potential propagator which would require the evaluation of two interactions with the potential, but rather as a higher-order remainder by taking the difference between the (unrenormalized) full bound self-energy term and the (unrenormalized) zero- and one-potential terms. Each term is expanded in terms of partial waves according to (6.23), and the difference is taken before summing over l. The evaluation of the matrix elements is performed in a similar way as for the transverse photon potential, with the spin-angular part treated analytically and the integrals over the radial coordinates and over the photon momentum treated numerically. An explicit coordinate-space expression for the many-potential term is given in Feynman gauge in Appendix D.

When extrapolating to continuous space and to an infinite summation limit in partial waves l, we obtain an uncertainty of the individual diagrams on the left-hand side in Figure 11 on the order of 0.1 percent for the self-energy correction. This uncertainty is of the same absolute magnitude as the very effects we wish to compute. An improvement can be achieved by carrying out the subtraction for each set of grid- and summation parameters before any extrapolation is performed. The

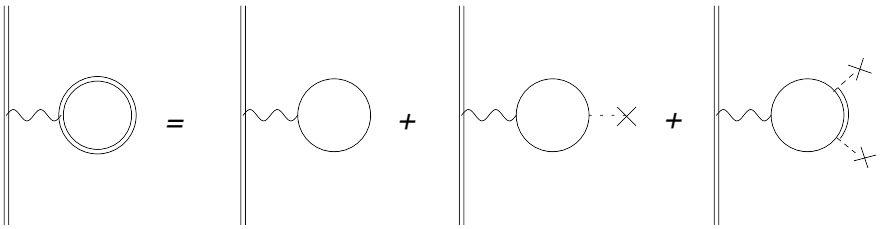


Figure 13: Expansion of the vacuum polarization operator in terms of scattering-order with the nuclear potential. Double-lines denote electrons propagating in the nuclear potential, while thin lines denote freely propagating electrons.

result can then be extrapolated with a relative uncertainty which is on the order of one percent for the combined effect of self-energy and correlation.

6.4.5 Vacuum Polarization

The two-electron matrix elements of the renormalized vacuum polarization potential are given by

$$\langle rs|U_{\mathrm{VP}}^{\mathrm{ren}}|tu\rangle = \delta_{u,s}\langle r|U_{\mathrm{VP}}^{\mathrm{ren}}|t\rangle + \delta_{t,r}\langle s|U_{\mathrm{VP}}^{\mathrm{ren}}|u\rangle. \tag{6.30}$$

Similary to the self-energy case (see Appendix B), the unrenormalized bound-state vacuum polarization can be expanded in terms of scattering order with the nuclear potential, resulting in a zero-, one-, and many-potential term (see Figure 13). The zero-potential term vanishes due to Furry's theorem [57], which states that the contribution from all fermion loops containing an odd number of vertices is zero. The one-potential term is divergent, but following a renormalization of the electron charge a finite remainder, known as the Uehling potential [31, 58], can be identified:

$$\begin{aligned} U_{\mathrm{VP}}^{\mathrm{Uehling}}(r) = &-\frac{e^2}{4\pi}\frac{\alpha}{\pi}\int_0^\infty dr' 4\pi r'^2 \rho_{\mathrm{nuc}}(r') \\ &\times \int_1^\infty dt\sqrt{t^2-1}\left(\frac{2}{3t^2}+\frac{1}{3t^4}\right) \\ &\times \frac{\sinh(4\pi t r_<\!/\lambda_{\mathrm{C}})}{4\pi t r_<\!/\lambda_{\mathrm{C}}}\frac{e^{-4\pi t r_>/\lambda_{\mathrm{C}}}}{r_>}. \end{aligned} \tag{6.31}$$

Here ρ_{nuc} is the nuclear charge-distribution and λ_{C} is the Compton wavelength of the electron. The Uehling potential gives the dominating contribution to the matrix elements of the renormalized vacuum polarization potential.

The remaining part, which is finite and unaffected by the renormalization, is known as the Wichmann-Kroll contribution [59] and contains all higher-order terms. It can be computed, in analogy with the self-energy many-potential term, as the difference between the full expression and the one-potential term. However, it can also be computed to good approximation using the analytical formulas given by Fainshtein *et al.* [60]. These analytical approximations were obtained by fitting, in a least-squares sense, finite series expansions in the radial coordinate r (including non-integral powers) to numerical results calculated from the definition (4.80). The relative level of accuracy obtained with this approximation is 10^{-4}, which is sufficient

for our purposes. By using the approximate formulas we avoid having to perform the explicit summation over states in the fermionic loop.

Thus, we obtain the matrix elements of the renormalized vacuum polarization potential as

$$\langle r|U_{\mathrm{VP}}^{\mathrm{ren}}|t\rangle = \langle r|U_{\mathrm{VP}}^{\mathrm{Uehling}}|t\rangle + \langle r|U_{\mathrm{VP}}^{\mathrm{W\text{-}K}}|t\rangle. \tag{6.32}$$

The Wichmann-Kroll potential $U_{\mathrm{VP}}^{\mathrm{W\text{-}K}}$ contributes less than 5% to the total energy shift in all cases considered in this work, which justifies its approximate treatment.

6.4.6 Model-Space Contributions

The model-space contributions (MSCs), are given by the terms involving energy derivatives of the perturbations in Eq. (6.14). We will in this work approximate the infinite sum of derivatives $\partial^n/\partial\mathcal{E}^n$ by the first ($n = 1$) term only. This derivative will affect the transverse-photon potential $V_{\mathrm{T}}(\mathcal{E})$ as well as the self-energy potential $\Sigma(\mathcal{E})$, but not the vacuum polarization which is energy-independent.

The energy-derivative of the transverse-photon potential affects only the energy denominators in Eq. (4.73), and the MSC can thus be computed with the same method as that for V_{T}, with the only difference being the form of the energy-denominators:

$$\frac{1}{\mathcal{E} - E_t - E_u - k} \to \frac{-1}{(\mathcal{E} - E_t - E_u - k)^2}. \tag{6.33}$$

It is not as straightforward to include the energy-derivative of the self-energy operator since it is UV-divergent even after renormalization (this divergence, which is located in the zero-potential term, can be seen by differentiating Eq. (B.3) with respect to p^0). At the two-photon level it can easily be shown, using the Ward identity (Eq. B.7), that this divergence cancels against a corresponding term in the *vertex correction* (see Figure 14). It has not been possible during the course of this work to explicitly demonstrate this cancellation in higher-order terms containing more than one Coulomb interaction. Specifically, at the three-photon level (two Coulomb interactions together with a self-energy or vertex photon) we find, assuming that the form of the regularized operators (Eqs. B.3 and B.4) remain the same in this order, that there is a mismatch by an overall factor of 2 in order to achieve cancellation — the divergence from the vertex correction terms is twice as large as that from the self-energy terms. We have also undertaken preliminary studies of these contributions based on the S-matrix formalism with Sucher's level shift formula, and they indicate the same problem; the derivation is however very complicated in this case. The reason for such a factor, if it turns out to be real, is unclear at this point. It is also not clear if it should affect only the divergent parts, or if the entire operators, including the finite contributions, should be modified. *We will in this work proceed by ignoring this difficulty, assuming that the cancellation of divergences does indeed take place in higher orders as it does at the two-photon level.* This is what one would expect from a comparison with free-electron QED, where (separable) self-energy and vacuum-polarization corrections in higher orders are given in terms of the renormalized operators. We consider the self-energy MSC together with the vertex correction and we include these effects only to the three-photon level, that is, terms containing precisely two Coulomb interactions.

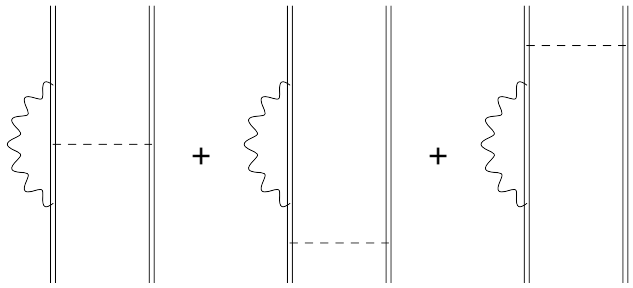


Figure 14: The complete, gauge-invariant Coulomb-screened self-energy at the two-photon level. The leftmost diagram is the vertex-correction. The two remaining terms contain the wavefunction-correction (only intermediate Q-space states) and the model-space contribution (MSC). The vertex correction has to be considered together with the MSC due to the cancellation of their respective divergent terms. (Taken from Ref. [38])

Our analysis of the Coulomb-screened self-energy at the two-photon level (see Table 2 in Chapter 8) suggests that in the Coulomb gauge we can obtain a reasonable approximation to the full evaluation of the self-energy MSC plus vertex-correction by simply neglecting the "higher-order terms" — the remainders after subtracting away the zero-potential terms. This is important since the full evaluation of the higher order term of the vertex-correction has to be performed individually for each combination of in- and outgoing two-electron states, which would become prohibitively time consuming in the general case. In contrast, the zero-potential terms can be computed without difficulty even in the fully correlated case, and this enables us to obtain approximate results for the combined correlation and self-energy MSC plus vertex-correction in the Coulomb gauge, again assuming that the cancellation of divergences proceeds in a straightforward way in the perturbation expansion. The Feynman gauge, on the other hand, would require evaluation also of the higher-order terms since there are very large cancellations among the terms in this gauge.

Our calculation of the vertex-correction and self-energy MSC proceeds as follows. The cancellation of UV-divergences between the vertex correction and self-energy MSC is handled with dimensional regularization (see Appendix B) following the usual nuclear-potential expansion of the bound electron propagators. The UV-divergent quantities are located in the zero-potential terms and the finite remainders after cancellation are computed in momentum-space as expectation values of the corresponding renormalized free-electron operators. The remaining higher-order contribution is computed in coordinate space from the bound-state QED Feynman rules as the difference between the diagrams with bound propagators and free propagators using a partial-wave expansion of the photon.

It is quite involved to analytically obtain the energy-derivative of the self-energy zero-potential term in Coulomb gauge due to the complicated form of the free electron self-energy operator in this gauge [61]. We find it more convenient to evaluate the derivative numerically as a finite-difference ratio. For the higher-order terms the energy-derivative of the self-energy can be obtained via a simple substitution of energy denominators in analogy with (6.33).

This concludes our discussion of the application of the Green's operator formal-

ism to compute the wavefunction and energy in the ground state of heliumlike ions. The numerical results will be presented in Section 8.1.

7 QED Corrections to Atomic Amplitudes

In this chapter we will consider the computation of QED corrections to transition amplitudes of atomic processes. Having developed the numerical machinery to include self-energy and vacuum polarization corrections to an atomic wavefunction in the previous chapter, we can easily obtain the corresponding corrections to a particular transition amplitude by using the corrected wavefunctions.

The atomic processes we will choose are radiative recombination and radiative decay of hydrogenlike ions. The former of these processes is the capture of a continuum electron by an ion together with the emission of a photon, and the latter is an atomic radiative transition where both the inital and final states are bound. The influence of the QED effects grows rapidly with the strength of the nuclear potential, and we will here consider hydrogenlike uranium since this is the most highly charged stable atomic system.

In the case of radiative recombination, we will study one-loop QED corrections to the transition amplitude for capture into the $1s$ state. From this amplitude we compute the corrections, due to the QED-perturbed bound-state wavefunction and energy, to the differential cross section and to the distribution of linear polarization of the emitted radiation. A theory for this process based on bound-state QED in the the two-times Green's function formalism was developed in Refs. [62] and [63] — some of the one-loop QED corrections were evaluated in [63]. The expressions for the one-loop QED corrections were also derived in our published paper, Ref. [37] by applying the connection between the Green's operator and the cross section derived therein (Eq. 5.45).

In the case of radiative decay we will compute the one-loop QED corrections, also here due to the perturbed wavefunctions and energies, to the amplitude of the $2p_{3/2} \to 1s$ transition. In particular we will be interested in the ratio $\tau_{\mathrm{M2}}/\tau_{\mathrm{E1}}$ of the magnetic quadrupole and electric dipole transition amplitudes, to which experimental access has recently been demonstrated [18, 64]. Previously, QED corrections to radiative decay in hydrogenlike ions have been considered in Ref. [65] and calculations of the one-loop QED corrections for the total decay rates of $n = 2$ states were reported in Ref. [66].

In both cases there are, apart from the corrections due to perturbed wavefunctions and energies, additional QED corrections such as the vertex correction to the emitted photon as well as the model-state contributions which we do not consider in this work.

The work discussed in this chapter is also described in our submitted manuscript, Ref. [39], and we must note that in some parts the presentation will be very similar.

7.1 Radiative Recombination

Radiative recombination occurs when a charged ion captures an electron from the continuum under the emission of a photon. The observables related to this process can be traced to the corresponding transition amplitude τ. The zeroth-order order amplitude for the capture of a continuum electron with (asymptotic) four-momentum p and spin projection μ into the bound state $|a\rangle$ of an initially bare

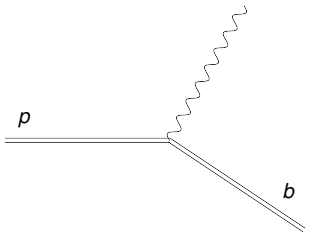


Figure 15: Feynman diagram for the radiative recombination process in the zeroth-order approximation. The continuum electron is denoted by p and the bound atomic electron is denoted by b. (Taken from Ref. [39])

atomic nucleus is given by [63, 67]

$$\tau^{(0)} = -e\langle a|\alpha^\nu A^*_\nu(\mathbf{k},\mathbf{x})|p,\mu\rangle\,, \tag{7.1}$$

where

$$A^\nu(\mathbf{k},\mathbf{x}) = \frac{\epsilon^\nu e^{i\mathbf{k}\cdot\mathbf{x}}}{\sqrt{2\omega(2\pi)^3}} \tag{7.2}$$

is the four-potential of the emitted photon with wavevector $\mathbf{k}$, energy $\omega = |\mathbf{k}|$, and polarization vector ϵ^ν. The Feynman diagram for the zeroth-order amplitude is shown in Figure 15.

The one-loop QED corrections to this amplitude are given in [37, 63]. The corrections from the electron self-energy (see Figure 16) are

$$\begin{aligned}\tau^{(1)}_{\rm SE} = -\Big[&\sum_{t\neq a}\frac{\langle a|\Sigma_{\rm ren}(E_a)|t\rangle\langle t|e\alpha^\nu A^*_\nu|p,\mu\rangle}{E_a-E_t} + \frac{1}{2}\langle a|\frac{\partial\Sigma_{\rm ren}}{\partial E}|a\rangle\langle a|e\alpha^\nu A^*_\nu|p,\mu\rangle\\ &+\sum_t\frac{\langle a|e\alpha^\nu A^*_\nu|t\rangle\langle t|\Sigma_{\rm ren}(p^0)|p,\mu\rangle}{p^0-E_t(1-i\varepsilon)} + \int d\mathbf{z}eA^*_\nu(\mathbf{z})\Lambda^\nu_{\rm B}(E_a,p^0,\mathbf{z})\\ &+(Z_2^{-1/2}-1)\langle a|e\alpha^\nu A^*_\nu|p,\mu\rangle\Big]\,,\end{aligned} \tag{7.3}$$

where $\Lambda^\nu_{\rm B}$ is the bound vertex-correction operator and Z_2 is a renormalization constant. The corresponding vacuum-polarization corrections are (see Figure 17)

$$\begin{aligned}\tau^{(1)}_{\rm VP} = -\Big[&\sum_{t\neq a}\frac{\langle a|U^{\rm ren}_{\rm VP}|t\rangle\langle t|e\alpha^\nu A^*_\nu|p,\mu\rangle}{E_a-E_t} + \sum_t\frac{\langle a|e\alpha^\nu A^*_\nu|t\rangle\langle t|U^{\rm ren}_{\rm VP}|p,\mu\rangle}{p^0-E_t(1-i\varepsilon)}\\ &+\int d\mathbf{z}\int d\mathbf{x}\int d\mathbf{y}eA^*_\nu(\mathbf{z})\psi^\dagger_a(\mathbf{x})\alpha^\lambda\psi_{p,\mu}(\mathbf{x})D_{\lambda\sigma}(\omega,\mathbf{x}-\mathbf{y})\Pi^{\sigma\nu}(\omega,\mathbf{y},\mathbf{z})\\ &+(Z_3^{-1/2}-1)\langle a|e\alpha^\nu A^*_\nu|p,\mu\rangle\Big]\,,\end{aligned} \tag{7.4}$$

where $U^{\rm ren}_{\rm VP}$ is the vacuum-polarization potential, $\Pi^{\sigma\nu}$ is the polarization tensor for the photon self-energy (see, e.g., [20]), and Z_3 is a renormalization constant.

The first term on the right-hand side of Eq. (7.3) can be computed with a self-energy-perturbed hydrogenic wavefunction,

$$|\delta a^{\rm SE}\rangle = \sum_{t\neq a}\frac{|t\rangle\langle t|\Sigma_{\rm ren}(E_a)|a\rangle}{E_a-E_t}, \tag{7.5}$$

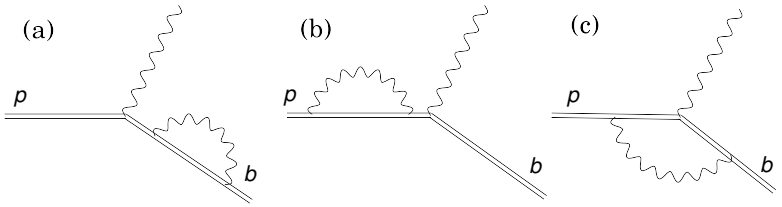


Figure 16: Feynman diagrams for the one-loop self-energy corrections to the radiative recombination process. (Taken from Ref. [39])

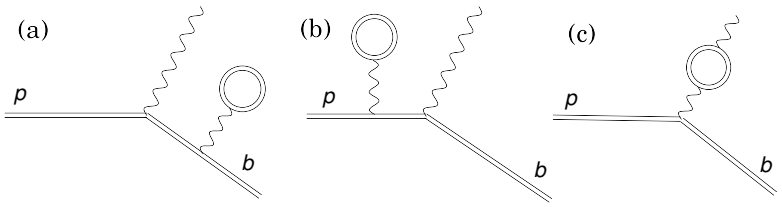


Figure 17: Feynman diagrams for the one-loop vacuum-polarization corrections to the radiative recombination process. (Taken from Ref. [39])

by making the substitution $\langle a| \to \langle \delta a^{\rm SE}|$ in Eq. (7.1). The corresponding term in the vacuum-polarization corrections can be treated similarly by the substitution $\langle a| \to \langle \delta a^{\rm VP}|$ with the VP-corrected wavefunction

$$|\delta a^{\rm VP}\rangle = \sum_{t\neq a} \frac{|t\rangle\langle t|U_{\rm VP}^{\rm ren}(r)|a\rangle}{E_a - E_t}. \tag{7.6}$$

These corrections to the bound-state wavefunction can readily be obtained using the numerical methods described in Sections 6.4.4 and 6.4.5.

In the present work we calculate only the first terms in the right-hand sides of Eqs. (7.3) and (7.4), which correspond to the diagrams in Figs. 16(a) and 17(a). In the case of vacuum-polarization, the diagram 17(b) could rather easily be evaluated as well. However, its contribution is expected [63] to be largely canceled by the corresponding self-energy diagram. The self-energy diagram is not so easy to evaluate due to the initial continuum state not being localized (see discussion in Section 6.4.4). Here we do not include any of these contributions. The remaining vacuum-polarization contribution can be expected to be small, since it vanishes in the Uehling approximation. However, the omitted self-energy terms in Eq. (7.3) are generally not small. The computational methods developed in this work are insufficient for the computation of these contributions, and we are thus forced to settle for an incomplete evaluation of the QED corrections to radiative recombination.

Let us now briefly describe how corrections to observable quantities can be obtained from the transition amplitude τ. The differential cross section for the emission of a photon with energy $\omega = |\mathbf{k}|$ into the solid-angle element $d\Omega$ is connected to the transition amplitude by the expression [63]

$$\frac{d\sigma}{d\Omega} = \frac{(2\pi)^4}{|\mathbf{v}|}\mathbf{k}^2\tau^*\tau\,, \tag{7.7}$$

where $\mathbf{v}$ is the velocity of the initial continuum electron. The expansion of the transition amplitude in terms of the fine-structure constant α,

$$\tau = \tau^{(0)} + \tau^{(1)} + \dots\,, \tag{7.8}$$

gives the zeroth-order differential cross section as

$$\frac{d\sigma^{(0)}}{d\Omega} = \frac{(2\pi)^4}{|\mathbf{v}|}\mathbf{k}^2 \tau^{(0)*}\tau^{(0)}\,. \tag{7.9}$$

The first-order correction (in α) to the cross section has two origins; one is due to the one-loop correction $\tau^{(1)}$ to the transition amplitude and the other is due to the one-loop shift of the energy of the emitted photon,

$$\begin{aligned}\frac{d\sigma^{(1)}}{d\Omega} =& \frac{(2\pi)^4}{|\mathbf{v}|}\mathbf{k}^2 \left(\tau^{(0)*}\tau^{(1)} + \tau^{(1)*}\tau^{(0)}\right) \\ &+ \frac{d\sigma^{(0)}}{d\Omega}\bigg|_{\omega=p^0-E_a^{\mathrm{QED},(1)}} - \frac{d\sigma^{(0)}}{d\Omega}\bigg|_{\omega=p^0-E_a}\,,\end{aligned} \tag{7.10}$$

where $E_a^{\mathrm{QED},(1)}$ is the energy of the state a corrected by one-loop QED effects and E_a is the zeroth-order energy of this state (without QED effects). Here, $\tau^{(1)}$ is given by Eqs. (7.3) and (7.4).

Apart from corrections to the cross section, we wish also to study how QED influences the polarization of the emitted radiation. In order to describe the polarization we make use of the so-called *Stokes parameters* P_1, P_2, and P_3. The first Stokes parameter P_1 can be accessed in experiment as

$$P_1 = \frac{I_{0^\circ} - I_{90^\circ}}{I_{0^\circ} + I_{90^\circ}}\,, \tag{7.11}$$

where I_x is the intensity of radiation whose linear polarizion vector makes an angle of x degrees relative to the reaction plane (the reaction plane is spanned by the momentum vector $\mathbf{p}$ of the incoming continuum electron and the wavevector $\mathbf{k}$ of the emitted photon). P_1 ranges from -1, where the polarization is completely perpendicular to the reaction plane, to $+1$ where it is completely parallel. P_2 can be constructed similarly to P_1 but the intensities should then be taken at angles of $x = 45^\circ$ and $x = 135^\circ$. As discussed in Ref. [67], in radiative recombination P_2 is proportional to the degree of spin-polarization of the incoming continuum electrons. Here we consider the initial electrons to be unpolarized, so that P_2 vanishes. The third Stokes parameter P_3 corresponds to the degree of circular polarization and will not be considered here.

In order to compute P_1 we express it in terms of the differential cross sections for two polarizations of the emitted radiation: one with the polarization parallel to the reaction plane, $(d\sigma/d\Omega)_\parallel$, and another with the polarization perpendicular to this plane, $(d\sigma/d\Omega)_\perp$. The resulting Stokes parameter P_1 can then be obtained as

$$P_1 = \frac{\left(\frac{d\sigma}{d\Omega}\right)_\parallel - \left(\frac{d\sigma}{d\Omega}\right)_\perp}{\left(\frac{d\sigma}{d\Omega}\right)_\parallel + \left(\frac{d\sigma}{d\Omega}\right)_\perp}\,. \tag{7.12}$$

The QED corrections to the cross section $d\sigma/d\Omega$ induce the corresponding corrections to P_1. In this work we will define the QED correction to P_1 as the difference of P_1 computed from the cross-section including the QED effects and without them,

$$\delta P_1 = P_1(\text{with QED}) - P_1(\text{without QED})\,. \tag{7.13}$$

Our results for the corrections discussed here will be given in Section 8.2.

7.2 Radiative Decay

As a second application of our QED corrected wavefunctions we consider the $2p_{3/2} \to 1s$ radiative decay in hydrogenlike uranium. Because of selection rules from angular momentum and parity conservation, this decay can proceed both via the $E1$ (electric dipole) and $M2$ (magnetic quadrupole) channels. It has recently been demonstrated that it is possible to gain direct experimental access to the ratio $\tau_{\mathrm{M2}}/\tau_{\mathrm{E1}}$ of the corresponding transition amplitudes [18]. We will here consider one-loop QED corrections to this ratio.

The separation of the radiative decay into different channels is a consequence of the expansion of the radiation field into so-called multipole components. We will not go into details about this expansion here, but simply take the relevant results from Ref. [68].

Recall first that the *helicity* λ of a particle is defined as the projection of its spin vector onto the propagation direction; the helicity of a real photon can only take the values $\lambda = \pm 1$. The spatial part of the four-potential (7.2) can for a particular photon helicity be written as [69]

$$\begin{aligned}\mathbf{A}_\lambda(\mathbf{k},\mathbf{r}) =& \frac{\boldsymbol{\epsilon}_\lambda e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{2\omega(2\pi)^3}} \\ =& \frac{1}{\sqrt{2\omega(2\pi)^2}} \sum_{L=0}^{\infty} \sum_{M=-L}^{L} i^L \sqrt{2L+1} D^L_{M\lambda}(\mathbf{z}\to\mathbf{k}) \left[\mathbf{A}^L_M(m) + i\lambda \mathbf{A}^L_M(e)\right] ,\end{aligned} \tag{7.14}$$

where, in the Coulomb gauge,

$$\mathbf{A}^L_M(m) = j_L(|\mathbf{k}|r)\mathbf{T}^{L,L}_M \tag{7.15}$$

is the magnetic $2L$-pole component and

$$\mathbf{A}^L_M(e) = \sqrt{\frac{L+1}{2L+1}} j_{L-1}(|\mathbf{k}|r)\mathbf{T}^{L,L-1}_M - \sqrt{\frac{L}{2L+1}} j_{L+1}(|\mathbf{k}|r)\mathbf{T}^{L,L+1}_M \tag{7.16}$$

is the electric $2L$-pole component. Both of these components are defined in terms of the so-called *vector spherical harmonics*

$$\mathbf{T}^{L,L'}_M = \sum_{m=-1}^{1} \langle L'M-m, 1m|LM\rangle Y^{L'}_{M-m}\boldsymbol{\xi}_m \tag{7.17}$$

where $\langle L'M-m,1m|LM\rangle$ is a Clebsch-Gordan coefficient, and where $\boldsymbol{\xi}_m$ are the unit spherical vectors

$$\boldsymbol{\xi}_0 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \qquad \boldsymbol{\xi}_{\pm1} = \frac{\mp1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm i \\ 0 \end{pmatrix}. \tag{7.18}$$

In Eq. (7.14), $D^L_{M\lambda}(\mathbf{z}\to\mathbf{k})$ is the Wigner rotation matrix which rotates the radiation field from the quantization axis $\mathbf{z}$ into the actual propagation direction $\mathbf{k}$. The magnetic quadrupole and electric dipole components of the radiation field are obtained from by Eq. (7.15) with $L=2$, and Eq. (7.16) with $L=1$, respectively.

The zeroth-order transition amplitudes of the $E1$ and $M2$ transitions can be shown to be proportional to the reduced matrix elements of the corresponding multipole components,

$$\begin{aligned} \tau^{(0)}_{\rm E1} &= C\,\langle a||\boldsymbol{\alpha}\cdot\mathbf{A}_1(e)||b\rangle\,, \\ \tau^{(0)}_{\rm M2} &= C\,\langle a||\boldsymbol{\alpha}\cdot\mathbf{A}_2(m)||b\rangle\,, \end{aligned} \tag{7.19}$$

where $|a\rangle$ is the $1s$ state and $|b\rangle$ is the $2p_{3/2}$ state. C is an overall factor which cancels in the ratio $\tau^{(0)}_{\rm E1}/\tau^{(0)}_{\rm M2}$ we are interested in.

In analogy with the case of radiative recombination considered above, the QED corrections to the amplitudes due to perturbations of the wavefunctions and energies can be expressed as

$$\begin{aligned} \tau^{(1)}_{\rm E1} =& C\,\Big[\langle\delta a^{\rm SE}||\boldsymbol{\alpha}\cdot\mathbf{A}_1(e)||b\rangle + \langle a||\boldsymbol{\alpha}\cdot\mathbf{A}_1(e)||\delta b^{\rm SE}\rangle \\ & \langle\delta a^{\rm VP}||\boldsymbol{\alpha}\cdot\mathbf{A}_1(e)||b\rangle + \langle a||\boldsymbol{\alpha}\cdot\mathbf{A}_1(e)||\delta b^{\rm VP}\rangle\Big]\,, \\ & + \tau^{(0)}_{\rm E1}\Big|_{\omega=E_a^{\rm QED,(1)}-E_b^{\rm QED,(1)}} - \tau^{(0)}_{\rm E1}\Big|_{\omega=E_a-E_b}\,, \end{aligned} \tag{7.20}$$

for $\tau^{(1)}_{\rm E1}$ and similarly for $\tau^{(1)}_{\rm M2}$. Here, the energy of the emitted photon is given by $\omega=|\mathbf{k}|=E_b-E_a$, and its value is shifted by the QED corrections to the bound-state energies.

Since this calculation involves an excited state as one of the model states, special care must be taken when computing the many-potential part of the self-energy correction. This part contains intermediate positive-energy states whose energy is smaller than the model-state energy, and this leads to the appearance of poles on the axis of integration over the virtual photon momentum. One must then consider so-called *Cauchy principal-value* integrals over these poles. The numerical implementation of these principal-value integrals is discussed in Appendix D.

As before, the correction (7.20) represents only a part of the total one-loop QED effect. The vertex contributions and the self-energy MSC [66, 70] are not calculated here.

8 Results and Discussion

In this chapter we will present our numerical results for the applications considered in this work. The results for the energy shift due to the combined effect of correlation and single-photon QED in the ground state of heliumlike ions are presented in Section 8.1; these results were also published in our paper, Ref. [38], and the presentation here will inevitably be very similar to the corresponding section in that paper.

In Section 8.2 we give results from the application of QED-corrected single-electron wavefunctions to the amplitudes and observables in radiative recombination as well as radiative decay of hydrogenlike uranium. These results are also described in our manuscript [39] which is submitted to Phys. Rev. A. Also in this case, the presentation given here will closely resemble the corresponding sections of that reference.

8.1 QED and Correlation in Heliumlike Ions

As stated in Section 6.3, one of the steps in our calculation of the combination of QED and correlation is the evaluation of two-photon diagrams where a single QED-photon is combined with a single Coulomb interaction (see Figure 11). The energy shift obtained from these diagrams can be compared to values in the literature and serve as a test of our method. In addition to this, since we in this work compute the self-energy correction in both Coulomb and Feynman gauge, it is interesting to compare in detail the various contributions in the two gauges. Such a comparison is presented in Table 2, which is taken from our published paper Ref. [38]. We note that the contributions in the two gauges are quite different. It could be argued that the Coulomb gauge behaves in a physically more intuitive way — in the sense that the higher-order terms act as small corrections to the zeroth-order terms. The Feynman gauge, by comparison, is characterized by a large degree of cancellation in general and large contributions from higher-order terms. It is, however, satisfying to find gauge-invariance for the final results. Our results are compared to values in the literature (obtained in the Feynman gauge) in Table 3. The last column of that table gives results for the self-energy screened, not only by a Coulomb interaction, but also by the transverse (Breit) interaction.

In Table 4 we give results for the energy-shift due to the combined effect of correlation and self-energy (effects beyond the two-photon level; see Eq. (6.16) and Figure 11). The calculation is performed both in the Coulomb and Feynman gauge to allow comparison. The contributions we have calculated behave quite differently in the two gauges and it is interesting to note the unphysical Z-behaviour of the Feynman gauge. In absolute terms, one would expect the combined self-energy and correlation (including MSC and vertex corrections) to scale roughly as Z^2 since the leading term differs by an extra $(1/Z)$ Coulomb interaction from the single-photon screened self-energy. This is not at all the case for the Feynman-gauge contributions we have calculated here — instead they actually *decrease* when Z increases. This suggests that a complete treatment including the higher-order MSC and vertex-correction terms is needed to get sensible results in this gauge. The corresponding

Table 2: Contributions to the Coulomb-screened self-energy shift at the two-photon level in the $1s^2$ state of some helium-like ions, in units of meV. "WF" refers to the part with only intermediate Q-states, "MSC" to the model-space contribution, and "VTX" to the vertex-correction. (Taken from Ref. [38])

Nuclear charge	Contribution	Coulomb gauge	Feynman gauge
$Z = 14$	WF zero-potential term	−64.7(7)	1498.3(7)
	WF one-potential term	2.70(2)	−1149.16(4)
	WF many-potential term	5.583(4)	−396.046(5)
	Sum	−56.4(7)	−46.9(7)
	MSC zero-potential term	−14.64(1)	3467.4(1)
	VTX zero-potential term	10.42(1)	−3327.6(1)
	MSC+VTX higher-order terms	−0.57(1)	−153.9(5)
	Sum	−4.79(3)	−14.1(7)
	Total Coulomb-screened self-energy	−61.2(7)	−61(1)
$Z = 18$	WF zero-potential term	−115.8(7)	1620.8(6)
	WF one-potential term	0.441(4)	−1218.16(4)
	WF many-potential term	11.111(5)	−489.559(6)
	Sum	−104.2(7)	−86.9(6)
	MSC zero-potential term	−24.79(2)	3819.0(1)
	VTX zero-potential term	16.21(2)	−3653.3(1)
	MSC+VTX higher-order terms	−1.07(2)	−192.2(6)
	Sum	−9.65(6)	−26.5(8)
	Total Coulomb-screened self-energy	−113.8(8)	−113(1)
$Z = 24$	WF zero-potential term	−221.4(6)	1722.3(3)
	WF one-potential term	−11.1(1)	−1279.37(5)
	WF many-potential term	24.059(7)	−617.076(9)
	Sum	−208.4(7)	−174.1(4)
	MSC zero-potential term	−43.22(4)	4164.5(1)
	VTX zero-potential term	24.12(4)	−3972.3(1)
	MSC+VTX higher-order terms	−2.16(4)	−246.9(8)
	Sum	−21.3(1)	−54.7(10)
	Total Coulomb-screened self-energy	−229.7(8)	−229(1)
$Z = 30$	WF zero-potential term	−360.4(4)	1758.44(7)
	WF one-potential term	−37.0(4)	−1322.11(5)
	WF many-potential term	43.33(1)	−733.10(1)
	Sum	−354.1(8)	−296.8(1)
	MSC zero-potential term	−63.6(1)	4362.4(1)
	VTX zero-potential term	28.3(1)	−4158.8(1)
	MSC+VTX higher-order terms	−3.71(6)	−299(1)
	Sum	−39.0(3)	−95.3(10)
	Total Coulomb-screened self-energy	−393(1)	−392(1)
$Z = 50$	WF zero-potential term	−1046.1(1)	1650.9(7)
	WF one-potential term	−307(3)	−1572.45(5)
	WF many-potential term	162.4(9)	−1088.9(1)
	Sum	−1191(4)	−1010.5(9)
	MSC zero-potential term	−117.1(2)	4458.9(1)
	VTX zero-potential term	−24.9(1)	−4328.7(1)
	MSC+VTX higher-order terms	−15.2(3)	−473(2)
	Sum	−157.2(6)	−342(2)
	Total Coulomb-screened self-energy	−1348(5)	−1352(3)

Table 3: Results for Coulomb-screened self-energy at the two-photon level obtained in this work are compared to values in the literature. For comparison the fifth column shows values for the complete screened self-energy, including also the transverse part of the exchanged photon. Units are meV. (Taken from Ref. [38])

Z	Coulomb gauge	Feynman gauge	Other authors	Other authors (including Breit-screening)
14	−61.2(7)	−61(1)		−59.6(2)[2]
18	−113.8(8)	−113(1)	−113.8[1]	−111.6[1],−111.60(2)[2]
24	−229.7(8)	−229(1)	−230.1[1]	−227.8[1]
30	−393(1)	−392(1)		−396.51(6)[2]
50	−1348(5)	−1352(3)		−1471.7(1)[2]

[1] Sunnergren [25].
[2] Artemyev *et al.* [43].

Coulomb-gauge values, on the other hand, show a Z-dependence which is closer to the expected one.

The energy-shifts due to the combined effect of QED and correlation are complied in Table 5 for all the single-photon QED perturbations considered in this work. The single transverse-photon exchange contributions were considered in the PhD thesis of Hedendahl [46] and numerical results are gathered from that work. The transverse interaction in Coulomb gauge can be shown to contain a part which is of instantaneous nature (the *instantaneous Breit interaction* [71]) whose contribution is given explicitly. We approximate the self-energy contribution as the sum of the calculated Coulomb-gauge terms in Table 4. We estimate the uncertainty of the self-energy contribution in the following way: At the two-photon level (Table 2) the higher-order terms represent roughly 10% of the total MSC+vertex contribution in Coulomb gauge. Based on this we assign an (arguably conservative) uncertainty estimate due to the uncalculated higher-order terms in the correlated case taken as 20% of the MSC+vertex zero-potential terms. To this we add the numerical uncertainty of the results in Table 4 and thus obtain the total uncertainty estimate. In the rightmost column of Table 5 we have summed the contributions from the self-energy, vacuum-polarization, and the retardation effect of the single-photon exchange, which can be considered as geniune QED effects. The magnitude and relative sign of the self-energy correction as compared to the vacuum-polarization agrees with what one finds in lower orders, and this further supports our approximative treatment of the self-energy in Coulomb gauge.

We have in this work only considered positive energies in the intermediate two-electron states (negative-energy states are however included in the self-energy and vacuum-polarization operators). The inclusion of negative-energy states in the perturbation expansion lies beyond the no-virtual-pair (NVP) approximation and are traditionally considered as a QED effects in the context of MBPT. This effect is not very important when considered together with only Coulomb interactions, but contributes significantly together with transverse-photon interactions (see e.g. [48]). Calculations of the combined effect of Coulomb-correlation and single-photon exchange together with virtual pairs based were performed in [46], and the magnitude

Table 4: Self-energy contributions to the combined QED-correlation energy shift beyond the two-photon level in the $1s^2$ state of some helium-like ions. The abbreviations are similar to those in Table 2. All values are given in units of meV. (Taken from Ref. [38])

Nuclear charge	Contribution	Coulomb gauge	Feynman gauge
$Z = 14$	Without MSC or vertex		
	- zero-potential term	3.47(3)	−164.82(3)
	- one-potential term	−0.0275(2)	71.80(3)
	- many-potential term	−0.451(3)	12.170(4)
	- sum	2.99(4)	−80.85(6)
	MSC zero-potential term	0.87	−30.7
	VTX zero-potential term	−0.63	66.5
	Total sum	3.23(4)	−45.05(6)
$Z = 18$	Without MSC or vertex		
	- zero-potential term	4.79(2)	−142.39(2)
	- one-potential term	0.143(1)	59.7(5)
	- many-potential term	−0.691(4)	11.569(3)
	- sum	4.24(3)	−71.1(5)
	MSC zero-potential term	1.16	−24.3
	VTX zero-potential term	−0.73	54.2
	Total sum	4.67(3)	−41.2(5)
$Z = 24$	Without MSC or vertex		
	- zero-potential term	6.77(2)	−118.482(5)
	- one-potential term	0.585(6)	47.8(4)
	- many-potential term	−1.104(6)	10.79(2)
	- sum	6.25(3)	−59.9(4)
	MSC zero-potential term	1.54	−17.6
	VTX zero-potential term	−0.76	41.6
	Total sum	7.03(3)	−35.9(4)
$Z = 30$	Without MSC or vertex		
	- zero-potential term	8.702(8)	−101.507(2)
	- one-potential term	1.22(1)	40.2(1)
	- many-potential term	−1.569(9)	10.250(6)
	- sum	8.36(3)	−51.1(1)
	MSC zero-potential term	1.82	−13.0
	VTX zero-potential term	−0.61	33.2
	Total sum	9.57(3)	−30.9(1)
$Z = 50$	Without MSC or vertex		
	- zero-potential term	14.823(2)	−69.641(1)
	- one-potential term	5.17(5)	29.88(2)
	- many-potential term	−3.30(2)	19.29(1)
	- sum	16.69(7)	−20.47(3)
	MSC zero-potential term	2.15	−4.9
	VTX zero-potential term	1.10	19.4
	Total sum	19.94(7)	−5.97(3)

Table 5: Contributions to the combined QED-correlation energy shift beyond the two-photon level in the $1s^2$-state of some heliumlike ions. The transverse-photon contributions are gathered from Ref. [46]. In the rightmost column we sum all contributions except the instantaneous Breit part. All values are given in meV. (Taken from Ref. [38])

Z	Transverse photon (instantaneous Breit)	Transverse photon (retardation effect)	Self-energy	Vacuum-polarization	Total QED-correlation effect
14	8.19	−1.86	3.2(1)	−0.136	1.2(1)
18	10.13	−2.73	4.7(1)	−0.225	1.7(1)
24	12.73	−4.16	7.0(2)	−0.402	2.5(2)
30	15.03	−5.71	9.6(3)	−0.639	3.3(3)
50	21.46	−11.47	19.9(7)	−2.093	6.3(7)

Table 6: Total combined QED-correlation effect in the $1s^2$-state of heliumlike ions compared to the "higher-order QED" effect from [43]. The second column gives our results in the no-virtual-pair approximation. The third column gives the estimated results after including virtual pairs. The rightmost column shows the uncertainties for the total ionization energies computed in [43]. In units of meV. (Adapted from Ref. [38])

Z	QED-correlation NVP	QED-correlation with VP (estimated)	Artemyev $\Delta E_{\rm ho}^{\rm QED}$ [43]	Total uncertainty in Ref. [43]
14	1.2(1)	1.0(1)	0.8	±0.2
18	1.7(1)	1.4(1)	0.9	±0.4
24	2.5(2)	2.0(2)		±0.8
30	3.3(3)	2.6(3)	−0.2	±1.9
50	6.3(7)	5.0(7)	−7.7(50)	±10

of the combined effect of retardation and correlation beyond the two-photon level (column 3 in Table 5) was there found to decrease by roughly 20% for all the values of Z considered. The corresponding correction from virtual pairs to the combined effect of correlation and self-energy/vacuum polarization has not yet been studied, but one might expect a correction of the same order — a reduction of the total QED-correlation effect by 20%.

In Table 6 our results for the combined correlation and QED shift are compared to the "higher-order QED correction" given in Artemyev *et al.* [43] which was calculated using the so-called *unified method* of Drake [72] and which approximates the correlational effects. The second column in Table 6 is taken from Table 5 and in the third column we have estimated the inclusion of virtual pairs by multiplying our results by a factor of 0.8 based on the discussion above. For $Z = 14$ and 18 the agreement with [43] is close but our results tend to be a bit larger. For $Z = 24$ no value is specified in [43], but we note that the result we obtain here is more than twice as large in magnitude as the uncertainty of the total ionization energy given in that work. A severe disagreement is seen for $Z = 30$ and $Z = 50$ which might be due to an increasing importance of relativistic effects in the electron correlation for heavier nuclei. These effects are included to a large extent in this work due to the use of a relativistic Dirac model-hamiltonian (Eq. 6.1) while the method of Drake [72] is based on a non-relativistic treatment of electron correlation. The results obtained in this work suggest that the combined effect of correlation and QED in the ground

state of heliumlike ions is underestimated in [43] for intermediate nuclear charges (at least for the cases $Z = 14$, $Z = 18$, and $Z = 30$).

We note also that the effects considered in this work cannot explain the alleged discrepancy between theory and experiment that was recently reported by Chantler *et al.* [73] in a compilation of measured $1s2p(^1P_1) \rightarrow 1s1s(^1S_0)$ transition energies in heliumlike ions. The corrections to the $1s2p$ state are expected to be much smaller than the corresponding corrections to the $1s1s$ state considered here, and our results may therefore be used as an indication of the magnitude and sign of the total correction to the transition energies. Based on this, we find that the correction is not only too small to account for any discrepancy as that claimed in [73], but also has the wrong sign.

8.2 QED Corrections to Atomic Amplitudes

In this section we will present the results from our application of QED corrected hydrogenic wavefunctions to observables in radiative recombination and radiative decay. Before we come to that, we begin with a presentation of the results for the self-energy correction to the hydrogenic wavefunctions.

8.2.1 Self-Energy Corrections to Hydrogenic Wavefunctions

Although the wavefunctions themselves are not observable, it might nevertheless be interesting to see how they are affected by the QED corrections, as this has not received as much attention in the past as has the corresponding binding energies. We will here focus on the self-energy correction, which is the numerically more difficult to calculate.

In Figure 18 we plot the self-energy correction to the radial $1s$ wavefunction in hydrogenlike uranium as computed in Feynman and Coulomb gauge. Note that the self-energy correction shifts the wavefunction outward radially, which corresponds to a less strongly bound electron in agreement with the positive sign of the associated energy shift (see, e.g., Ref. [30]). As expected, the correction to the wavefunction is not gauge-invariant since it represents only a part of the one-loop QED corrections to observable quantities. Nevertheless, the difference between the corrections in the two gauges is quite small and both corrections display a very similar radial behaviour.

In Figure 19 we compare the contributions from the zero-, one-, and many-potential terms to the wavefuction-correction in the two gauges, for the large and small components. It is interesting to note that the one-potential term is roughly the same in both gauges, whereas the zero-potential and many-potential terms play opposite roles in Coulomb and Feynman gauge. Furthermore, in Coulomb gauge most of the effect comes from the zero- and one-potential terms with the many-potential term acting as a relatively small correction.

Figure 20 shows the self-energy correction in Feynman gauge to the $2p_{3/2}$ radial wavefunction in hydrogenlike uranium. Again, we see that the self-energy correction shifts the wavefunction outward in accordance with the positive energy shift. The typical size of the correction is one order of magnitude smaller than that for the $1s$ state (Figure 18). This reflects the fact that an electron in the $2p$-state is not as

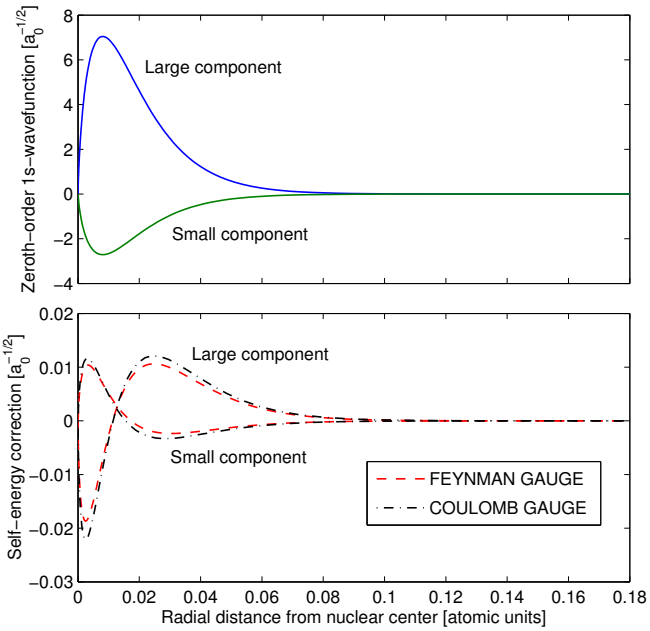


Figure 18: The zeroth-order radial wavefunction of the $1s$ state (top) and the self-energy correction in Feynman gauge and Coulomb gauge (bottom) for $Z = 92$. The correction shifts the wavefunction outward radially which corresponds to a less strongly bound electron. The radial unit is the Bohr radius a_0 and the wavefunctions are given in units of $1/\sqrt{a_0}$. (Taken from Ref. [39])

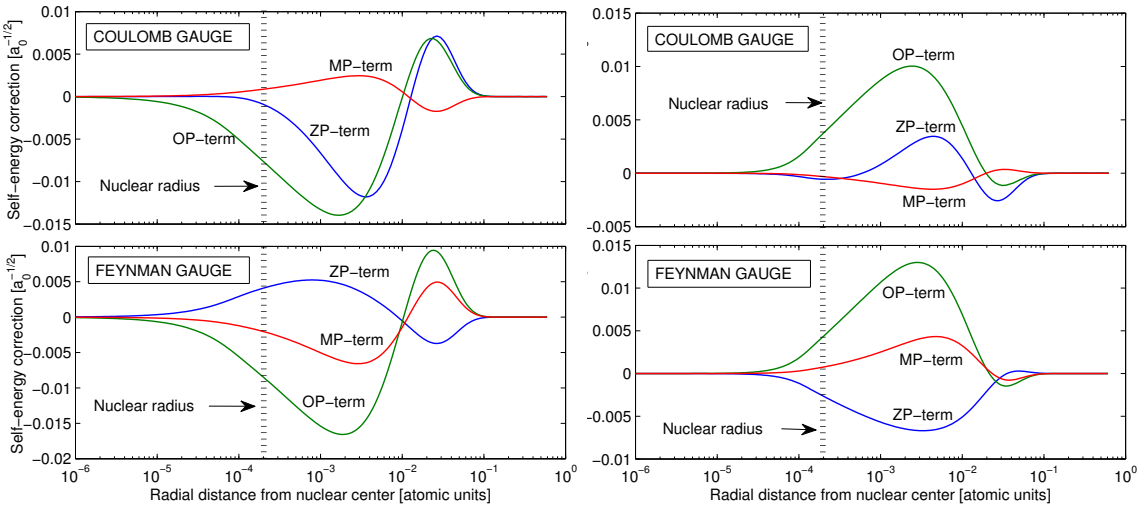


Figure 19: A comparison of the contributions from the different terms in the potential-expansion of the total self-energy correction to the large component (left) and small component (right) of the $1s$ wavefunction for $Z = 92$, as calculated in the Feynman and Coulomb gauges. The x-axes are logarithmic in order to enhance the nuclear region. Units are the same as in Fig. 18.(Adapted from Ref. [39])

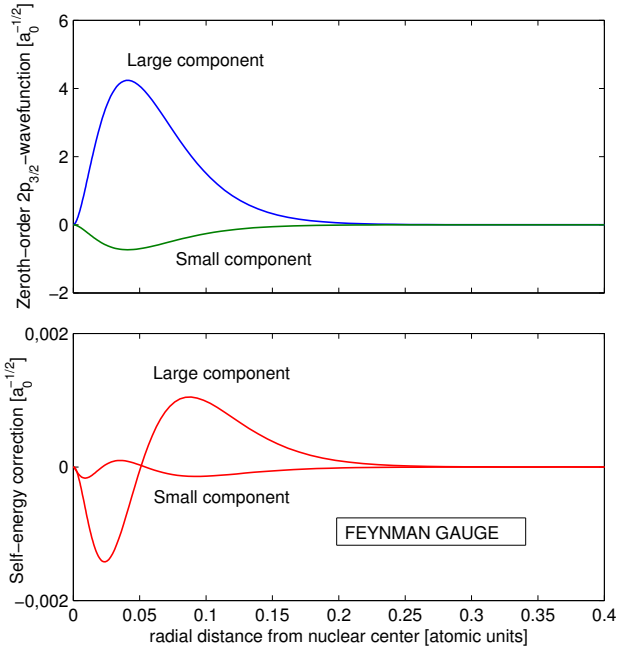


Figure 20: The zeroth-order radial $2p_{3/2}$-wavefunction (top) and the self-energy correction in Feynman gauge (bottom) for $Z = 92$. Units are the same as in Fig. 18.(Taken from Ref. [39])

likely to be found near the nuclear region (where QED effects are the largest) as it is in the $1s$-state.

8.2.2 Radiative Recombination

Having presented the self-energy corrections to the hydrogenic wavefunctions, we proceed now with the results for K-shell radiative recombination of hydrogenlike uranium. Figure 21 shows our results for the self-energy correction to the differential cross section for radiative recombination of an electron into the $1s$ state of an (initially bare) uranium nucleus. The results are given in the rest frame of the initial electron. This corresponds to the laboratory frame in an experiment where an incoming energetic bare nucleus captures a quasi-free electron from a stationary target. Our Feynman-gauge results are in good agreement with the results from Ref. [63], also obtained in Feynman gauge.

In Figure 22 we plot the sum of the QED corrections computed in this work to the differential cross section. The vacuum polarization corrections are computed in the Uehling approximation. In contrast to Ref. [63], we did not include any corrections associated with a finite energy-distribution of the initial continuum electrons. Thus, our results are valid for the case in which the energy spread of the continuum electrons is much smaller than the energy resolution of the photon detection. Our results are not fully gauge invariant since we have not included all QED corrections of first order in α.

The corrections we have computed here behave qualitatively in the same way in both gauges and the difference between them is relatively small. However, this can

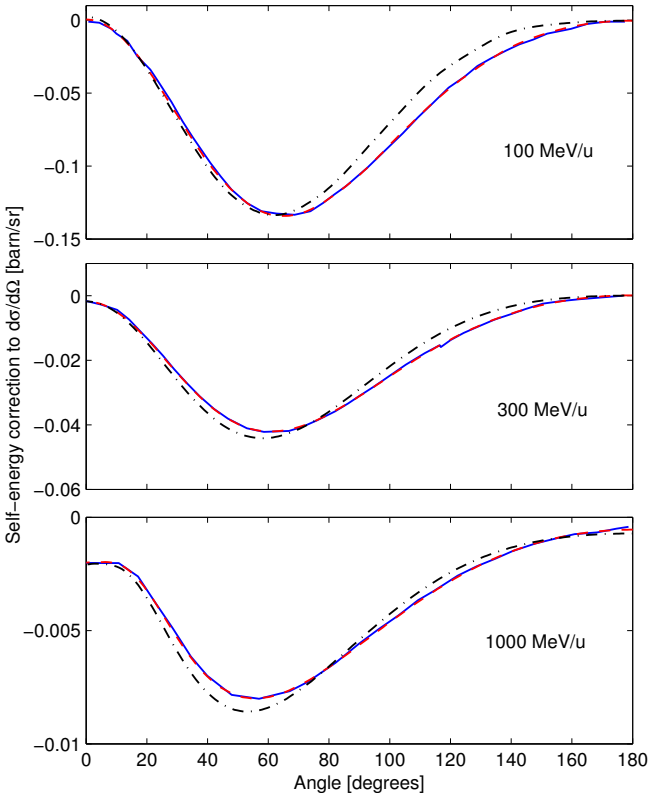


Figure 21: Self-energy wave-function and energy-shift corrections to the differential cross section of radiative recombination of an electron into the $1s$ state of bare uranium in the rest frame of the initial-state electron, for three different energies of the projectile (incoming bare uranium). The lines are: Feynman gauge (dashed red), Coulomb gauge (dash-dotted black), in comparison with the previous results by Shabaev *et al.* [63] (solid blue). (Taken from Ref. [39])

not be taken as an indication that the uncalculated QED effects are small. Indeed, it may happen that they are also similar in the two gauges considered here. The obtained plots suggest that the relative size of the QED effects to the differential cross section grows with increasing energy (albeit quite slowly) and that these effects are most pronounced at a photon observation angle of roughly 60 degrees.

The polarization of the emitted radiation (the Stokes parameter P_1) is plotted as a function of observation angle in Fig. 23, together with the QED correction δP_1 as defined in Eq. (7.13). For all three projectile energies we observe that the result of the correction is that the curve gets shifted toward smaller angles. The largest QED correction appears in the lowest of the three projectile energies and in the very forward direction, at an angle of just 1 degree (see inset in the lower leftmost plot in Figure 23).

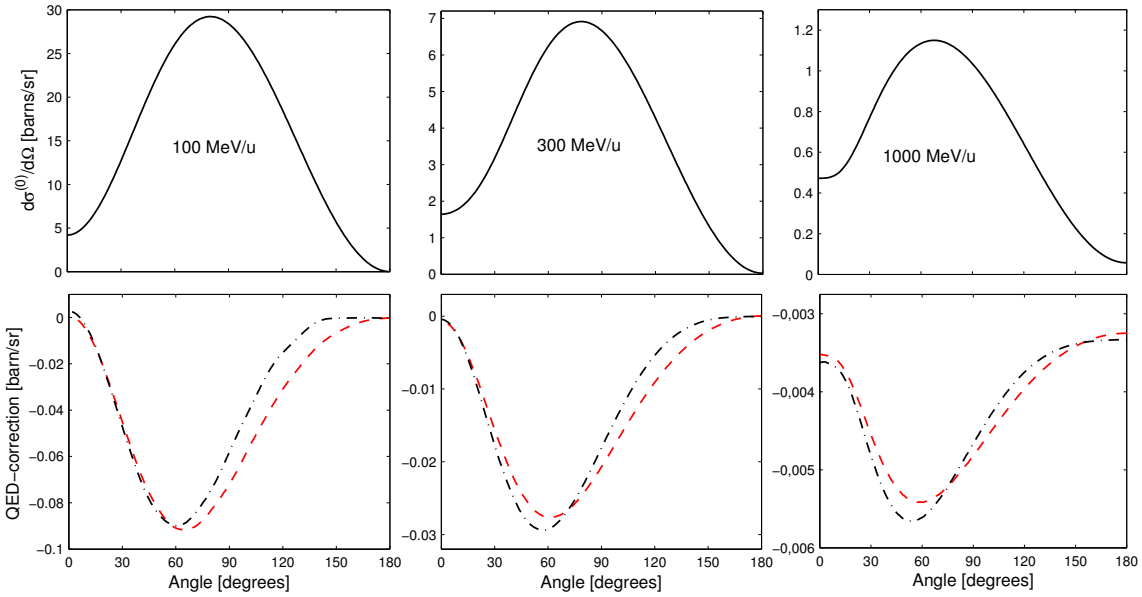


Figure 22: Differential cross section of radiative recombination of an electron into the $1s$ state of bare uranium in the rest frame of the continuum electron, for the ion-projectile energies 100 MeV/u, 300 MeV/u, and 1 GeV/u, respectively. Upper plots: zeroth-order cross section. Lower plots: the QED corrections (the self-energy and vacuum-polarization bound wave-function corrections and the correction due to the shift of the bound-state energy) in the Feynman gauge (dashed red line) and in the Coulomb gauge (dash-dotted black line). (Taken from Ref. [39])

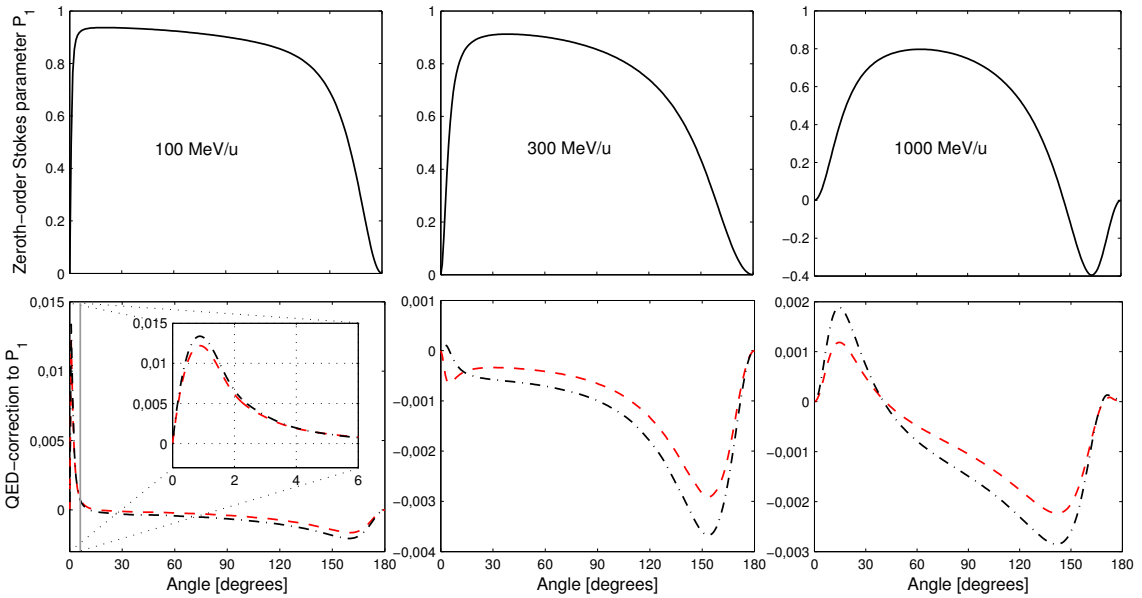


Figure 23: Polarization of the emitted radiation in the rest frame of the continuum electron, for the three ion-projectile energies. Upper plots: Stokes parameter P_1 in the zeroth-order approximation. Lower plots: the same kinds of QED corrections as in Figure 22. In the plot for 100 MeV/u we have inserted a zoom-in of the narrow region around the 1-degree direction. (Taken from Ref. [39])

Table 7: Individual contributions to the electric dipole and magnetic quadrupole reduced matrix elements and for the ratio of the corresponding transition amplitudes, for the $2p_{3/2} \to 1s$ transition in U^{91+}, in atomic units. SE denotes the self-energy corrections calculated in the Feynman gauge, VP denotes the vacuum-polarization corrections. Note that the specified uncertainties represent only the numerical errors of the calculated contributions; the uncertainty due to missing QED effects is not included. (Taken from Ref. [39])

Contribution	$\langle a\|\|\boldsymbol{\alpha}\cdot\mathbf{A}_1(e)\|\|b\rangle$	$\langle a\|\|\boldsymbol{\alpha}\cdot\mathbf{A}_2(m)\|\|b\rangle$	τ_{M2}/τ_{E1}
Dirac (point-like nucleus)	0.0740699(1)	0.0062527(1)	0.084416(1)
Dirac (finite nuclear size, $R_{\rm nuc} = 5.863$ fm)	0.0741350(2)	0.0062458(1)	
SE: $2p_{3/2}$ wavefunction correction	−0.0000293(1)	−0.000000815(1)	
SE: $1s$ wavefunction correction	0.00008898(1)	0.00002677(2)	
VP: $2p_{3/2}$ wavefunction correction	0.000001016(1)	0.0000000415(1)	
VP: $1s$ wavefunction correction	−0.00001272(1)	−0.000006495(2)	
VP+SE: correction from energy shift	0.000041106(1)	−0.000028075(1)	
Sum QED + nuclear size	0.0742241(3)	0.0062372(1)	0.084032(2)
Difference			−0.000384(3)

8.2.3 Radiative Decay

Finally, we present our results for the transition-amplitude ratio in radiative decay. In Table 7 we give numerical values of the $E1$ and $M2$ reduced matrix elements for the $2p_{3/2} \to 1s$ transition in hydrogenlike uranium, as well as the ratio of the corresponding transition amplitudes, $\tau_{\rm M2}/\tau_{\rm E1}$. The first row shows results obtained with point-nucleus Dirac energies and wavefunctions. The second row shows the corresponding results obtained with an extended nucleus (see Table 1). In the next rows we give the individual QED corrections and the final results, obtained in the Feynman gauge. The vacuum-polarization corrections here include also the Wichmann-Kroll contribution, in contrast to our results for radiative recombination.

As can be seen from Table 7, the finite nuclear size and the QED effects together induce a correction of -0.46% to the ratio of the $E1$ and $M2$ amplitudes. This is smaller by almost a factor of 40 than the experimental error given in Ref. [18]. Our present calculation is not complete and we cannot make a quantitative prediction for the total shift, it does however seem unlikely that QED effects can influence the interpretation of the experimental results in Ref. [18].

9 Summary and Outlook

In this work we have implemented a numerical procedure in which the electron self-energy and vacuum polarization, which are single-particle (radiative) QED effects, are included in a perturbation expansion of atomic wavefunctions. Using the QED-perturbed wavefunctions obtained with this procedure, we have computed corrections to four observable quantities in atomic physics: i) the energy-shift of the ground state in heliumlike ions due to the combination of electron correlation and single-photon QED, ii) those parts of the one-loop QED corrections to the differential cross section in radiative recombination of hydrogenlike uranium which are derivable from perturbed bound-state wavefunctions and energies, iii) the corresponding corrections to the angular distribution of linear polarization in the same process, and iv) the corresponding corrections to the ratio of the electric dipole and the magnetic quadrupole transition amplitudes in the $2p_{3/2} \to 1s$ radiative decay of hydrogenlike uranium. The evaluation of the self-energy corrections, which has constituted the main effort in this work, have been performed in both the Feynman and Coulomb gauges. Emphasis has been placed on the comparison of the various contributions to the self-energy corrections in these two gauges.

The numerical procedure we have implemented in this work is based on the recently developed theoretical framework known as the "covariant evolution-operator formalism" [13, 14, 16, 17]. In this work, special emphasis has been placed on the so-called Green's operator $\mathcal{G}$, which can be constructed from the covariant evolution-operator. This operator acts as a wave operator — that is, an operator which generates exact states from their corresponding zeroth-order approximations. In contrast to the standard wave operator defined in many-body perturbation theory, the Green's operator is able to handle energy-dependent perturbations such as the equivalent potentials derived from QED. By numerically constructing this operator we have been able to compute corrections to the atomic wavefunctions and associated observables.

We have also derived a relation between the so-called effective interaction, which is constructed from $\mathcal{G}$, and the forward scattering amplitude which can be used to compute cross sections for collision processes (Eq. 5.45). This relation is valid also when bound states are present, in contrast to the standard S-matrix approach which leads to singularities due to intermediate states degenerate with the inital state.

Part I of the thesis was devoted to a presentation of the theoretical background needed for the inclusion of QED effects into the atomic wavefunction. This began in Chapter 2 with a brief review of Dirac's relativistic single-electron theory. This theory is in many respects the main building block of our approach, since the bound-state solutions obtained therein serve both as model states (zeroth-order approximations) for our sought exact states, as well as provide a complete set of basis functions used in the subsequent perturbation expansion.

In Chapter 3 we discussed the basics of standard many-body perturbation theory, which is a framework for constructing exact states out of their corresponding model states under the influence of energy-independent (instantaneous) perturbations.

Chapter 4 was devoted to a formulation of the basic theory of bound-state QED. We also gave expressions for the energy-dependent equivalent potentials which can

be used to describe the photon-mediated interactions among the atomic electrons.

Finally, in Chapter 5 we described the covariant evolution-operator formalism and the Green's operator which can be used to construct a generalization of the standard many-body perturbation theory which is valid for energy-dependent perturbations. We also showed that the Green's operator can be used to compute cross sections for collision processes involving bound states.

In Part II we considered applications of the theory presented in Part I and described their numerical implementation. Chapter 6 descibes the application of the energy-dependent many-body perturbation theory to compute the combined effect of electron correlation and QED effects in heliumlike ions. We studied the energy shift in the ground state due to terms in the perturbation expansion containing at least two Coulomb interactions together with a single "QED photon" (including radiative effects).

In Chapter 7 we discussed the application of QED-perturbed hydrogenic wavefunctions to compute one-loop QED corrections to transition amplitudes and corresponding observables in basic atomic processes. The two processes we considered were radiative recombination and radiative decay of hydrogenlike uranium. For radiative recombination, we computed some of the one-loop corrections to the differential cross section as well as to the distribution of polarization in the emitted radiation. For the case of radiative decay, we computed similar corrections to the ratio of the electric dipole and magnetic quadrupole transition amplitudes in the $2p_{3/2} \to 1s$ decay.

In Chapter 8 we presented and discussed our numerical results. The results presented were taken from our published paper (Ref. [38]) as well as our submitted manuscript (Ref. [39]). For the energy shift due to combined correlation and QED in heliumlike ions our results indicate that this effect is slightly underestimated in the predicted energy for the ground state based on state-of-the-art two-photon QED calculations in Ref. [43], at least for the nuclear charges $Z = 14$, $Z = 18$, and $Z = 30$. Furthermore, we found that an approximative treatment of the combined effect of correlation and self-energy in Feynman gauge, where we kept only the zeroth-order terms in a potential-expansion of the so-called vertex and model-space contribution, gave results which displayed an unphysical scaling with the nuclear charge Z. This was not the case for the corresponding results in Coulomb gauge. Based on the analysis of these effects at the two-photon level (Table 2), we argued that the higher-order terms play a significant role in the Feynman gauge, while these terms act only as minor corrections in Coulomb gauge.

For the radiative recombination studies, we found good agreement with previously reported Feynman-gauge results for the differential cross section [63] for initially bare uranium. We also found that the distribution of linear polarization of the emitted radiation experienced a shift toward smaller angles due to the QED effects considered here. For our study of the amplitude-ratio in radiative decay of hydrogenlike uranium, we found that the QED corrections considered in this work were of the expected order of magnitude ($\approx \alpha$) and smaller by about a factor of 40 than the present experimental error [18]. For both radiative recombination and radiative decay we found that the difference between the self-energy corrections in Coulomb and Feynman gauge considered in this work was quite small.

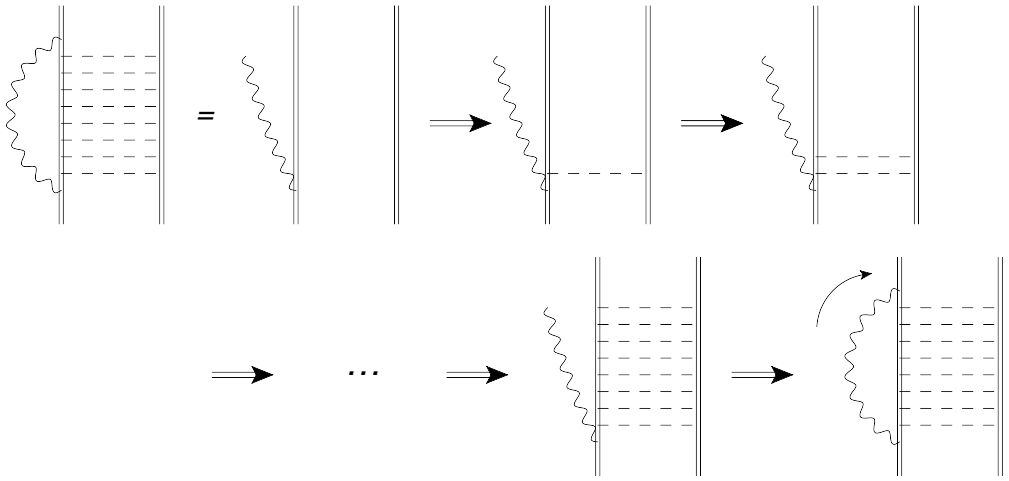


Figure 24: Coulomb interactions can be generated while the photon is uncontracted by iteratively solving a generalized pair-equation including a photon with momentum **k**. When sufficiently many Coulomb iterations have been performed, the photon is "closed" by acting with a photon absorption-operator and integrating over **k**.

Let us end with a few comments on possible future developments of the research described here.

Although the magnitude of our results for combined correlation and QED in the ground state of heliumlike ions indicate that the corresponding effect in excited states would be too small to be relevant for present-day experimental studies of transition energies, it might nevertheless become important in the future if experimental and theoretical uncertainties continue to improve. In order to see how the actual transition energies are influenced, one must of course also compute the corresponding corrections to the excited states, for example the $1s2p$ states. The $^3P_1$ and $^1P_1$ states are in this case described by model states which are linear combinations of the $1s2p_{1/2}(J = 1)$ and $1s2p_{3/2}(J = 1)$ basis states, and this would require an application of the full formalism for extended model spaces developed in Ref. [16], which we have not considered here.

We have in this work considered electron correlation described by arbitrarily many Coulomb interactions *before and after* the equivalent single-photon potentials derived from QED. This means that we neglect the correlation taking place *while* the QED photon is "in the air". It would, for example, be desirable to compute the effect from arbitrarily many Coulomb interactions appearing inside the self-energy loop (which can be considered as a higher-order vertex correction). This can in principle be accomplished with the use of so-called *open virtual photons* which are described in Ref. [14]. Here, an exchanged photon is treated as two separate local perturbations and by defining a generalized pair equation which is valid in an extended (Fock) state space allowing for uncontracted photons, one can use iterative solution methods similar to those described in Chapter 6 to produce Coulomb interactions appearing together with the uncontracted photon (see Figure 24). Such an approach was considered in the PhD thesis of Daniel Hedendahl [46] for the case of correlation and single-photon exchange. A significant contribution

from this "simultaneous correlation" was found which resulted in a reduction of the correlation effect by roughly 50%. In this work we have included this effect for the self-energy to first order (in the from of a vertex correction to a single Coulomb interaction), and although it is unlikely the higher-order contributions would be very large, an explicit evaluation of this effect would be of interest.

Furthermore, a complete treatment of electron correlation would of course require an unrestricted inclusion of negative-energy states as well as the Breit part of the interelectronic interaction. This is, however, not feasible with computing resources available at present.

A problem more fundamental in character, which also seems more urgent, is the apparent lack of cancellation of the UV divergences in higher orders between the vertex correction and self-energy model-space contribution. This problem was discussed in Section 6.4, and as mentioned there, our preliminary attemps to derive the expression for the self-energy model-space contribution (also known as the *reference state contribution*) at the three-photon level using the S-matrix formalism together with Sucher's formula have indicated the same problem in that framework. It would be very interesting to apply the third available method for bound-state QED, namely the two-time Green's function method of Shabaev, to this problem.

Finally, definitive quantitative results for the one-loop QED corrections to the dynamical processes considered in Chapter 7 would require the evaluation of the vertex correction as well as the self-energy model-space contribution.

10 Acknowledgements

During the course of the work described in this thesis, I have had support from a number of people. I will try to remember all of them here.

First and foremost, I would like to thank my supervisor Priv.-Doz. Dr. Andrey Surzhykov, whose support in the form of a well-balanced mix between encouragement and motivational challenge has been very valuable. For his devotion to the success of my research as well as to my personal wellbeing I am truly grateful.

I wish also to express my sincere gratitude to Priv.-Doz. Dr. Zoltán Harman for agreeing to be one of the referees of this thesis.

The evaluation of the combined effect of correlation and QED in heliumlike systems has been performed in close collaboration with Prof. Em. Ingvar Lindgren and Assoc. Prof. Sten Salomonson at the University of Gothenburg in Sweden. Their support, moral as well as technical, has been crucial to the success of this project, and I would like to express my deepest gratitude to the both of them. It has been a true privilege to work in your group. I would also like to thank Dr. Daniel Hedendahl, a previous member of the Gothenburg group, for invaluable support and stimulating discussions.

The evaluation of the QED corrections to atomic transition amplitudes were carried out in collaboration with Dr. Anton N. Artemyev and Dr. Vladimir A. Yerokhin, and I am indebted to them for sharing with me glimpses of their vast wisdom regarding quantum electrodynamics.

I would also like to thank the current and former colleagues at the Physikalisches Institut of the University of Heidelberg for creating a pleasant, stimulating, and open workplace: Dr. Armen Hayrapetyan, Dr. Oliver Matula, Dr. Thorsten Jahrsetz, Dr. Sean McConnell, Oleksiy Kovtun, Holger Jörg, Shintan Shah, Allison Pinto, Dr. Zhimin Hu, and Priv.-Doz. Dr. Stanislav Tashenov.

My stay at the Department of Physics at the University of Gothenburg has been made very pleasant, stimulating, and educational due to the following people: Erik Werner, Jonas Einarsson, Dr. Johan Rohlén, Dr. Anton Lindahl, Prof. Dag Hanstorp, Dr. Jonathan Weidow, Jakob Welander, Jan-Åke Wiman, Mats Rostedt, and those I forgot.

I would like to thank the "Heidelberg Graduate School for Fundamental Physics" and the "Helmholtz Graduate School for Hadron and Ion Research" for providing stimulating courses and educational opportunities. In particular I am grateful for the extensive help and support offered by the people employed under these organizations.

I would like to express my deepest gratitude for the consistent support and encouragement I have received throughout all my life from my family — my father Alf Holmberg, my mother Anne-Marie Holmberg, and my brother Andreas Holmberg with family.

Finally, to the love of my life and the mother of my son — the wonderful Emelie Lindquist — your unconditional love and support, during the good times as well as the bad, is a true blessing.

Appendices

A Derivation of the Relation Between the Forward Scattering Amplitude and the Effective Interaction

We will here derive the relation (5.45) for a single-electron system. This derivation follows that of our published paper, Ref. [37], closely.

First, we define the *reaction operator* $\mathcal{R}$ by [13, 14, 16]

$$W_{\text{eff}} = P\left[i\frac{\partial}{\partial t}\mathcal{G}(t,-\infty)\right]_{t=0} P \equiv P\mathcal{R}P. \tag{A.1}$$

The single-electron Green's operator can be written in the form (assuming that it contains at least one interaction)

$$\begin{aligned}\mathcal{G}(t,-\infty) &= \int d^3\mathbf{x}\int d^4y\ \psi^\dagger(x)S_{\text{F}}(x,y)\mathcal{F}\psi(y)\\ &= \sum_{m,n} a_m^\dagger a_n \int dt_y \int \frac{d\omega}{2\pi}\ \langle m|S_{\text{F}}(\omega)\mathcal{F}|n\rangle e^{-it(\omega-E_m)}e^{-it_y(E_n-\omega)}\end{aligned} \tag{A.2}$$

where $a^\dagger$ and a are the electron creation and annihilation operators of Eq. (4.21), and where spatial integration is implied in the matrix element. We will now demonstrate that the unknown operator $\mathcal{F}$ is equal to the reaction operator $\mathcal{R}$. We begin by performing the integrals over t_y and ω, which gives

$$\mathcal{G}(t,-\infty) = \sum_{m,n} e^{-it(E_n-E_m)}a_m^\dagger a_n\langle m|\Gamma(E_n)\mathcal{F}|n\rangle = \sum_{m,n}\frac{e^{-it(E_n-E_m)}}{E_n-E_m}a_m^\dagger a_n\langle m|\mathcal{F}|n\rangle, \tag{A.3}$$

using the explicit form of the resolvent (Eq. 3.37). Taking the time-derivative of this equation, evaluated at $t=0$, we find

$$\left[\frac{\partial}{\partial t}\mathcal{G}(t,-\infty)\right]_{t=0} = -i\sum_{m,n} a_m^\dagger a_n\langle m|\mathcal{F}|n\rangle = -i\mathcal{F} \tag{A.4}$$

which, using Eq. (A.1), implies that $\mathcal{F}=\mathcal{R}$.

If we now let $t\to+\infty$ in (A.2), the final electron propagator can be removed according to Eq. (5.5), and we find

$$\mathcal{G}(\infty,-\infty) = -i\int d^4y\ \psi^\dagger(y)\mathcal{R}\psi(y) = -i\sum_{m,n} a_m^\dagger a_n\int dt_y\langle m|\mathcal{R}|n\rangle e^{-it_y(E_n-E_m)}. \tag{A.5}$$

Performing the time integral yields

$$i\mathcal{G}(\infty,-\infty) = 2\pi\delta(E_{\text{in}}-E_{\text{out}})\mathcal{R}, \tag{A.6}$$

and according to (A.1) we then have

$$Pi\mathcal{G}(\infty,-\infty)P = 2\pi\delta(E_{\text{in}}-E_{\text{out}})W_{\text{eff}}. \tag{A.7}$$

In the absence of bound states, there are no intermediate model-space singularities and the Green's operator is in this case equal to the covariant evolution-operator. Furthermore, since the covariant evolution-operator for infinite times $U_{\mathrm{cov}}(\infty, -\infty)$ is identical to the S-matrix operator, we have the following relation in the free-electron case (again, we are neglecting the zeroth-order part which does not contain any interaction):

$$Pi(S-1)P = -PTP = Pi\mathcal{G}(\infty, -\infty)P = 2\pi\delta(E_{\mathrm{in}} - E_{\mathrm{out}})W_{\mathrm{eff}}, \tag{A.8}$$

This is just Eq. (5.45) and serves as an alternative definition of the forward scattering amplitude which is valid also in the bound-state case, provided that W_{eff} is constructed from the Green's operator or some equivalent method capable of handling model-space singularities.

B Renormalization of the Bound-State Self-Energy

The first difficulty one encounters when trying to compute matrix elements of the renormalized bound-state self-energy operator is how to accomplish the renormalization. Various methods have been applied in the past [74–76] but here we will follow the approach originally conceived by Brown *et al.* [77] and improved by Blundell and Snyderman [54]. This approach relies on an expansion of the bound-state electron propagator in terms of the scattering order with the nuclear potential (see Figure 25):

$$\begin{aligned} S_{\mathrm{F}}^{\mathrm{bound}}(\mathbf{x},\mathbf{y},z) &= S_{\mathrm{F}}^{\mathrm{free}}(\mathbf{x},\mathbf{y},z) + \int d^3\mathbf{x}_1\; S_{\mathrm{F}}^{\mathrm{free}}(\mathbf{x},\mathbf{x}_1,z)V(\mathbf{x}_1)S_{\mathrm{F}}^{\mathrm{free}}(\mathbf{x}_1,\mathbf{y},z) \\ &\quad + \int d^3\mathbf{x}_1 \int d^3\mathbf{x}_2\; S_{\mathrm{F}}^{\mathrm{free}}(\mathbf{x},\mathbf{x}_1,z)V(\mathbf{x}_1)S_{\mathrm{F}}^{\mathrm{bound}}(\mathbf{x}_1,\mathbf{x}_2,z)V(\mathbf{x}_2)S_{\mathrm{F}}^{\mathrm{free}}(\mathbf{x}_2,\mathbf{y},z) \end{aligned} \tag{B.1}$$

where $V = -eV_{\mathrm{nuc}}$ is the nuclear potential and where the free propagator $S_{\mathrm{F}}^{\mathrm{free}}$ is constructed from solutions to the Dirac equation in the limit that $V_{\mathrm{nuc}} \to 0$ everywhere.

Inserting this expansion into the definition of the self-energy operator (Eq. 4.77), we can write the matrix elements of the renormalized self-energy operator as[4]

$$\begin{aligned} \langle t|\Sigma_{\mathrm{ren}}|r\rangle &= \langle t|(\Sigma - \gamma^0\delta m)|r\rangle \\ &= \langle t|\gamma^0\Sigma^{\mathrm{free}}|r\rangle + \langle t|\gamma^0\Lambda^{0,\mathrm{free}}V|r\rangle + \langle t|\Sigma^{\mathrm{MP}}|r\rangle - \delta m\langle t|\gamma^0|r\rangle. \end{aligned} \tag{B.2}$$

Here, Σ^{free} is the free-electron self-energy operator which comes from the first term on the right-hand side of (B.1), and $\Lambda^{0,\mathrm{free}}$ is the time component of the free-electron vertex-correction operator which comes from the second term. The remaining part Σ^{MP} is known as the "many-potential term" and will be discussed further below.

The operators Σ^{free} and $\Lambda^{0,\mathrm{free}}$ are defined in terms of divergent integrals, and in order to evaluate them in a meaningful way one must introduce some kind of regularization which renders the integrals finite. We will here make use of the method of dimensional regularization introduced by T'Hooft and Veltmann [78] (see e.g. [20] for an excellent overview of this method). This method relies upon modifying the dimensionality of spacetime to $D = 4-\varepsilon$ where ε is a small parameter. The integrals which are divergent for $D = 4$ are convergent for finite ε. The divergent parts are proportional to $1/\varepsilon$ and can be shown to cancel when renormalization is taken into account, after which the $\varepsilon \to 0$ limit can be restored.

After the regularization has been imposed, the operators Σ^{free} and $\Lambda^{0,\mathrm{free}}$ can in momentum space be written in the form [20]

$$\Sigma^{\mathrm{free}}(p) = \delta m + A(\gamma^\mu p_\mu - m) + \Sigma_{\mathrm{ren}}^{\mathrm{free}}(p) \tag{B.3}$$

$$\Lambda^{0,\mathrm{free}}(p,q) = B\gamma^0 + \Lambda_{\mathrm{ren}}^{0,\mathrm{free}}(p,q) \tag{B.4}$$

[4] An additional γ^0 matrix appears in the matrix elements of the free-electron operators, since they are usually defined with respect to outgoing states given by the Dirac adjoint $\bar{\psi} = \psi^\dagger\gamma^0$.

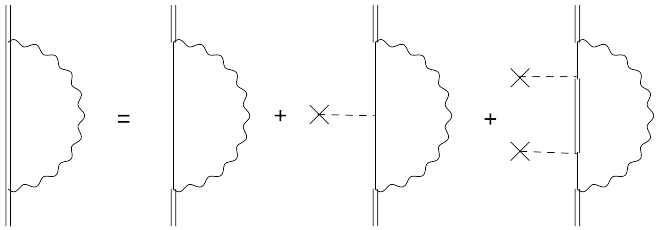


Figure 25: Expansion of the bound electron self-energy in terms of scattering-order with the nuclear Coulomb potential. Here, the thin lines refer to freely propagating electrons, while the double lines denote electrons propagating in the nuclear potential. (Taken from Ref. [39])

where δm, A, and B are divergent constants (containing terms proportional to $1/\varepsilon$). Inserting these forms into the expansion (B.5) we find for the divergent contributions (Σ^{MP} is finite):

$$\langle t|\gamma^0[\delta m + A(\gamma^\mu p_\mu - m)]|r\rangle - e\langle t|B\gamma^0\gamma^0 V_{\mathrm{nuc}}|r\rangle - \delta m\langle t|\gamma^0|r\rangle. \tag{B.5}$$

and we can directly see that the δm terms cancel. Furthermore, by using the Dirac equation in the presence of the nuclear potential,

$$(\gamma^\mu p_\mu - m)|r\rangle = -e\gamma^0 V_{\mathrm{nuc}}|r\rangle, \tag{B.6}$$

together with the so-called *Ward identity* (see, e.g., Ref. [20])

$$\frac{\partial\Sigma}{\partial p_\mu} = -\Lambda^\mu \tag{B.7}$$

which implies that $B = -A$, we find that all divergent terms cancel in the matrix element $\langle t|\Sigma_{\mathrm{ren}}|r\rangle$. The finite parts can be written as a zero-potential, a one-potential, and a many-potential term:

$$\langle t|\Sigma_{\mathrm{ren}}|r\rangle = \Sigma^{\mathrm{ZP}}_{tr} + \Sigma^{\mathrm{OP}}_{tr} + \Sigma^{\mathrm{MP}}_{tr} \tag{B.8}$$

where

$$\Sigma^{\mathrm{ZP}}_{tr} = \langle t|\gamma^0\Sigma^{\mathrm{free}}_{\mathrm{ren}}|r\rangle \tag{B.9}$$

is the matrix element of the renormalized free-electron self-energy operator and

$$\Sigma^{\mathrm{OP}}_{tr} = -e\langle t|\gamma^0\Lambda^{0,\mathrm{ren}}_{\mathrm{free}}V_{\mathrm{nuc}}|r\rangle \tag{B.10}$$

where $\Lambda^{0,\mathrm{ren}}_{\mathrm{free}}$ is the time-component of the renormalized free-electron vertex correction operator. The remaining many-potential term can be computed directly from the rules of bound-state QED.

C Evaluation of the Zero- and One-Potential Terms

We shall here evaluate the spin-angular parts of the zero- and one-potential matrix elements of the renormalized self-energy operator. We will consider general incoming and outgoing Fourier-transformed wavefunctions, which are of the form

$$\Phi(\mathbf{p}) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int d^3\mathbf{x}\; e^{-i\mathbf{p}\cdot\mathbf{x}} \Phi(\mathbf{x}) = \begin{pmatrix} P(|\mathbf{p}|)\chi_\kappa^m(\hat{p}) \\ Q(|\mathbf{p}|)\chi_{-\kappa}^m(\hat{p}) \end{pmatrix} \tag{C.1}$$

where $\hat{p}$ is the unit vector $\mathbf{p}/|\mathbf{p}|$. The coordinate-space function $\Phi(\mathbf{x})$ may be a hydrogenic energy eigenfunction or a correction to such a function, but may also be the single-coordinate representation of the resolvent for a fixed outgoing $\mathbf{x}'$, as in Eqs. (6.28) and (6.29).

Zero-Potential Term

We consider first the zero-potential term, which is given by the renormalized free-electron self-energy operator. In Coulomb gauge this operator is of the form [29]

$$\Sigma_{\text{free}}^{\text{ren}}(p) = A(\gamma^\mu p_\mu - m) + B\boldsymbol{\gamma}\cdot\mathbf{p} + Cm \tag{C.2}$$

where A, B, and C are scalar functions of the dimensionless variable

$$\rho = 1 - \frac{p^2}{m^2} = 1 - \frac{\mathcal{E}^2}{m^2} + \frac{\mathbf{p}^2}{m^2}. \tag{C.3}$$

Explicit expressions for these functions are given in [61].

The matrix element we wish to compute is

$$\langle\Phi_1|\gamma^0\Sigma_{\text{free}}^{\text{ren}}|\Phi_2\rangle = \int_0^\infty d|\mathbf{p}|\;\mathbf{p}^2 \int d\Omega\;\Phi_1^\dagger(\mathbf{p})\gamma^0\left[A(\gamma^\mu p_\mu - m) + B\boldsymbol{\gamma}\cdot\mathbf{p} + Cm\right]\Phi_2(\mathbf{p}). \tag{C.4}$$

The angular integral of the Cm-term, which is diagonal in spinor indices, can be obtained immediately:

$$\begin{aligned} Cm\int d\Omega\Phi_1^\dagger(\mathbf{p})\gamma^0\Phi_2(\mathbf{p}) &= Cm\int d\Omega\left(P_1P_2\chi_{\kappa_1}^{m_1,\dagger}\chi_{\kappa_2}^{m_2} - Q_1Q_2\chi_{-\kappa_1}^{m_1,\dagger}\chi_{-\kappa_2}^{m_2}\right) \\ &= \delta_{\kappa_1,\kappa_2}\delta_{m_1,m_2}Cm(P_1P_2 - Q_1Q_2). \end{aligned} \tag{C.5}$$

By using the explicit forms of the γ matrices (Eqs. 2.3 - 2.6), as well as the identities

$$(\boldsymbol{\sigma}\cdot\mathbf{p})\chi_\kappa^m(\hat{p}) = -|\mathbf{p}|\chi_{-\kappa}^m(\hat{p}), \tag{C.6}$$

$$\chi_\kappa^{m,\dagger}(\boldsymbol{\sigma}\cdot\mathbf{p}) = -|\mathbf{p}|\chi_{-\kappa}^{m,\dagger}(\hat{p}), \tag{C.7}$$

the angular integral of the A-term gives

$$\begin{aligned} &\int d\Omega\;\Phi_1^\dagger(\mathbf{p})\gamma^0 A(\gamma^\mu p_\mu - m)\Phi_2(\mathbf{p}) \\ &\qquad = \delta_{\kappa_1,\kappa_2}\delta_{m_1,m_2}A\left[P_1P_2(p^0 - m) + Q_1Q_2(p^0 + m) + |\mathbf{p}|(P_1Q_2 + Q_1P_2)\right] \end{aligned} \tag{C.8}$$

The remaining term can be evaluated similarly;

$$B\int d\Omega\ \Phi_1^\dagger(\mathbf{p})\gamma^0\boldsymbol{\gamma}\cdot\mathbf{p}\Phi_2(\mathbf{p}) = -B|\mathbf{p}|(P_1Q_2+Q_1P_2), \tag{C.9}$$

and the final matrix element is given in terms of an integral over $|\mathbf{p}|$:

$$\begin{aligned}\langle\Phi_1|\gamma^0\Sigma^{\rm ren}_{\rm free}|\Phi_2\rangle = \int_0^\infty d|\mathbf{p}|\mathbf{p}^2\big\{&Cm(P_1P_2-Q_1Q_2)+|\mathbf{p}|(A-B)(P_1Q_2+Q_1P_2)\\ &+A[P_1P_2(p^0-m)+Q_1Q_2(p^0+m)]\big\}.\end{aligned} \tag{C.10}$$

One-Potential Term

The one-potential term is a bit more involved since it is nondiagonal in momenta. We will here need the scalar component of the Coulomb-gauge vertex function, which is of the form [56]

$$\begin{aligned}\Lambda^{0,\rm ren}_{\rm free}(\mathbf{p},\mathbf{q},\mathcal{E}) = \frac{\alpha}{4\pi}\Big[&\gamma^0h_1+(\boldsymbol{\gamma}\cdot\mathbf{p}\gamma^0\boldsymbol{\gamma}\cdot\mathbf{q})h_2+(m\boldsymbol{\gamma}\cdot\mathbf{p}\gamma^0)h_3+(m\gamma^0\boldsymbol{\gamma}\cdot\mathbf{q})h_4\\ &+(\boldsymbol{\gamma}\cdot\mathbf{p})h_5+(\boldsymbol{\gamma}\cdot\mathbf{q})h_6+mh_7\Big]\end{aligned} \tag{C.11}$$

where h_i are (lengthy) scalar functions of $\mathcal{E}=p^0=q^0$, $|\mathbf{p}|$, $|\mathbf{q}|$ and $\cos\vartheta$ where ϑ is the angle between $\mathbf{p}$ and $\mathbf{q}$. Their explicit expressions are given in Ref. [56].

After performing the spinor operations on $\Phi_1^\dagger(\mathbf{p})$ and $\Phi_2(\mathbf{q})$, we can write the relevant matrix element at

$$\begin{aligned}\frac{4\pi}{\alpha}\Phi_1^\dagger(\mathbf{p})\gamma^0\Lambda^{0,\rm free}_{\rm ren}\Phi_2(\mathbf{q}) =&\chi_\kappa^{m\dagger}(\hat{p})\chi_\kappa^m(\hat{q})\Big[h_1P_1P_2+h_2pqQ_1Q_2-h_3mpQ_1P_2\\ &-h_4mqP_1Q_2-h_5pQ_1P_2-h_6qP_1Q_2+h_7mP_1P_2\Big]\\ &+\chi_{-\kappa}^{m\dagger}(\hat{p})\chi_{-\kappa}^m(\hat{q})\Big[h_1Q_1Q_2+h_2pqP_1P_2+h_3mpP_1Q_2\\ &+h_4mqQ_1P_2-h_5pP_1Q_2-h_6qQ_1P_2-h_7mQ_1Q_2\Big]\end{aligned} \tag{C.12}$$

where $p=|\mathbf{p}|$ and $q=|\mathbf{q}|$ and where $P_1=P_1(p)$, $Q_1=Q_1(p)$, $P_2=P_2(q)$, and $Q_2=Q_2(q)$.

For the spherically symmetric nuclear potential, the vertex operator is indendent of the magnetic quantum number m. This means that a summation over m combined with division by $2j+1$ is an identity operation. The can then use the identity

$$\frac{1}{2j+1}\sum_{m=-j}^{j}\chi_\kappa^{m\dagger}(\hat{p})\chi_\kappa^m(\hat{q}) = \frac{1}{4\pi}\mathcal{P}_{|\kappa+1/2|-1/2}(\cos\vartheta), \tag{C.13}$$

where $\mathcal{P}_l(x)$ is the lth Legendre polynomial in x, to get rid of the explicit dependence on the individual angles $\hat{p}$ and $\hat{q}$.

Furthermore, we need the expression for the Fourier-transformed nuclear potential for an extended nucleus. This depends on $k=|\mathbf{k}|$ where $\mathbf{k}=\mathbf{q}-\mathbf{k}$, and can be written as

$$(2\pi^2)V_{\rm nuc}(k) = -\frac{Z\alpha}{k^2}+\int_0^{R_{\rm nuc}}dr\ r^2j_0(kr)\left[V_{\rm nuc}(r)+\frac{Z\alpha}{r}\right]. \tag{C.14}$$

This means that the angular dependence of both the vertex operator and the nuclear potential reduces to a dependence on $\cos\theta$, and the domain of integration in the matrix element becomes

$$\int d^3\mathbf{p} \int d^3\mathbf{q} \to 8\pi^2 \int_0^\infty dp\, p^2 \int_0^\infty dq\, q^2 \int_{-1}^1 d(\cos\vartheta). \tag{C.15}$$

We thus end up with the following expression for the matrix element:

$$\begin{aligned}
-e\langle\Phi_1|\gamma^0\Lambda^{0,\mathrm{ren}}_{\mathrm{free}}V_{\mathrm{nuc}}|\Phi_2\rangle = -\frac{e\alpha}{2}\int_0^\infty dp\, p^2 \int_0^\infty dq\, q^2 \int_{-1}^1 d(\cos\vartheta)\, V_{\mathrm{nuc}}(p,q,\cos\vartheta) \\
\Big\{\mathcal{P}_{|\kappa+1/2|-1/2}(\cos\vartheta)\Big[h_1P_1P_2 + h_2pqQ_1Q_2 - h_3mpQ_1P_2 \\
- h_4mqP_1Q_2 - h_5pQ_1P_2 - h_6qP_1Q_2 + h_7mP_1P_2\Big] + \\
\mathcal{P}_{|-\kappa+1/2|-1/2}(\cos\vartheta)\Big[h_1Q_1Q_2 + h_2pqP_1P_2 + h_3mpP_1Q_2 \\
+ h_4mqQ_1P_2 - h_5pP_1Q_2 - h_6qQ_1P_2 - h_7mQ_1Q_2\Big]\Big\}
\end{aligned} \tag{C.16}$$

There is an integrable Coulomb singularity at $p = q$ in this expression, which we separate out by writing

$$-e\langle\Phi_1|\gamma^0\Lambda^{0,\mathrm{ren}}_{\mathrm{free}}V_{\mathrm{nuc}}|\Phi_2\rangle = \int_0^\infty dp\, p^2 \int_0^\infty dq\, q^2 \int_{-1}^1 dz\, \frac{\tilde{g}(p,q,z)}{k^2}. \tag{C.17}$$

with $z \equiv \cos\theta$. This singularity is handled with the variable transformations

$$v = -\frac{1}{2pq}\ln(k^2) = -\frac{1}{2pq}\ln(p^2+q^2-2pqz) \tag{C.18}$$

$$y = p - q \tag{C.19}$$

$$x = p + q \tag{C.20}$$

suggested by Blundell [53]. The integral then takes the form

$$-e\langle\Phi_1|\gamma^0\Lambda^{0,\mathrm{ren}}_{\mathrm{free}}V_{\mathrm{nuc}}|\Phi_2\rangle = \frac{1}{2}\int_0^\infty dx \int_{-x}^{x} dy \int_{v_{\min}}^{v_{\max}} dz\, \tilde{g}\left(\frac{x+y}{2}, \frac{x-y}{2}, z(x,y,v)\right) \tag{C.21}$$

where $v_{\min} = -\ln(x)/pq$ and $v_{\max} = -\ln(y)/pq$. The divergence at $y \to 0$ is removed by the further substitution

$$s = y\ln\left(\frac{y}{x}\right) - y \tag{C.22}$$

for $|y| < x/10$.

The corresponding evaluations of the zero- and one-potential terms in Feynman gauge are performed in Ref. [55].

D Principal-Value Integrals in the Many-Potential Term

We will here consider the integration over pole-states in the many-potential term of the matrix element of the self-energy operator. This section follows, nearly word-for-word, the corresponding part of our submitted manuscript [39].

The many-potential term can be written in coordinate space as a sum over the orbital angular momentum l of the virtual photon:

$$\Sigma_{rt}^{\mathrm{MP}} = \sum_{l=0}^{\infty} \Sigma_{rt}^{\mathrm{MP},l} \,. \tag{D.1}$$

Each l-term can be calculated using the expansion of the self-energy operator (Figure 25) as

$$\Sigma_{rt}^{\mathrm{MP},l} = \langle r|\Sigma|t\rangle^l - \langle r|\Sigma_{\mathrm{free}}|t\rangle^l - \langle r|\Lambda^0_{\mathrm{free}}(-e)V_{\mathrm{nuc}}|t\rangle^l \,. \tag{D.2}$$

Here, all operators on the right-hand side are unrenormalized and constructed in coordinate space.

The Feynman-gauge expression for the many-potential term in this scheme is

$$\begin{aligned}\Sigma_{rt}^{\mathrm{MP},l} = -\frac{\alpha}{\pi}(2l{+}1) \int k\, dk \Bigg\{ & \sum_m \frac{\langle r|\alpha^\mu j_l(kr_1)\mathbf{C}^l|m\rangle\langle m|j_l(kr_2)\mathbf{C}^l\alpha_\mu|t\rangle}{\mathcal{E} - E_m - \mathrm{sign}(E_m)k} \\ & - \sum_p \frac{\langle r|\alpha^\mu j_l(kr_1)\mathbf{C}^l|p\rangle\langle p|j_l(kr_2)\mathbf{C}^l\alpha_\mu|t\rangle}{\mathcal{E} - E_p - \mathrm{sign}(E_p)k} \\ & - \sum_{p,q} \frac{\langle t|\alpha^\mu j_l(kr_1)\mathbf{C}^l|p\rangle\langle p|(-e)V_{\mathrm{nuc}}|q\rangle\langle q|j_l(kr_2)\mathbf{C}^l\alpha_\mu|t\rangle}{[\mathcal{E} - E_p - \mathrm{sign}(E_p)k][\mathcal{E} - E_q - \mathrm{sign}(E_q)k]}\, F \Bigg\}\end{aligned} \tag{D.3}$$

where $\mathcal{E}$ is the energy-parameter of the self-energy operator; for hydrogenlike ions it is equal to the model state energy and for heliumlike ions it is equal to the model state energy minus the energy of the "spectator electron". The states $|m\rangle$ are generated in the nuclear potential and $|p\rangle$ and $|q\rangle$ refer to states generated in the limit $Z \to 0$. The function F is given by

$$F = 1 + [\mathrm{sign}(E_p) - \mathrm{sign}(E_q)]\frac{k}{E_p - E_q} \tag{D.4}$$

and ensures proper treatment of negative-energy states in the third term (the "vertex" term). The corresponding expression for $\Sigma_{rt}^{\mathrm{MP},l}$ in Coulomb gauge can be found in Ref. [30].

The first term on the right-hand side of Eq. (D.3) (the "bound" term) contains a pole on the k-axis whenever there is an intermediate state $|m_0\rangle$ with a positive energy $E_{m_0} < \mathcal{E}$. This situation can appear if the model state is not the ground state, and the appearance of the pole is related to the spontaneous decay of the excited state. In this case one has to perform a numerical Cauchy principal-value (CPV) integral[5] over k when evaluating Eq. (D.3).

[5]The Cauchy principal-value integral of a function $f(x)$ over an interval $[a, b]$ which contains a pole at $x = \omega$ is defined here as the limit of $\left[\int_a^{\omega-\epsilon} dx\, f(x) + \int_{\omega+\epsilon}^b dx\, f(x)\right]$ as $\epsilon \to 0^+$.

In order to accomplish the CPV integration in a numerically stable way, we first note that the integrand of the bound term for the intermediate pole-state $|m_0\rangle$ is of the form

$$f(k) = \frac{g(k)}{\omega - k}\,, \tag{D.5}$$

where the pole is located at $\omega = \mathcal{E} - E_{m_0}$. Next we separate out the singular part:

$$f(k) = f(k) - \frac{g(\omega)}{\omega - k} + \frac{g(\omega)}{\omega - k} \equiv h(k) + \frac{g(\omega)}{\omega - k}\,, \tag{D.6}$$

where now

$$h(k) = \frac{g(k) - g(\omega)}{\omega - k} \tag{D.7}$$

contains no poles and can be integrated numerically without difficulty. The CPV integral of the remaining term can be evaluated analytically over a suitable interval $[0, C]$ that includes ω to give

$$\int_0^C dk \frac{g(\omega)}{\omega - k} = -g(\omega)\ln(|1 - \frac{C}{\omega}|)\,. \tag{D.8}$$

The total integral thus becomes

$$\int_0^\infty dk\ f(k) = -g(\omega)\ln(|1 - \frac{C}{\omega}|) + \int_0^C dk\ h(k) + \int_C^\infty dk\ f(k). \tag{D.9}$$

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